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Photocatalyzed oxidation and mineralization of branched and oxidized C4 and C5 aliphatic acids in UV-irradiated aqueous titania dispersions Adsorption and degradation dynamics

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Abstract

The photocatalyzed degradation and mineralization of branched C4 and C5 acids {2-methylpropanoic acid (2-MPA), 2-methylbutanoic acid (2-MBA), 3-methylbutanoic acid (3-MBA), and trimethylacetic acid (TMA)} and oxidized C4 and C5 carboxylic acids {e.g., 2-hydroxybutanoic acid (2-HBA), 2-hydroxy-2-methylbutanoic acid (2-OH-2-MBA), 2-hydroxyvaleric acid (2-HVA), and 2-ketovaleric acid (2-KVA)} were examined in UV-irradiated air-equilibrated aqueous TiO_2 dispersions to assess: (a) the extent of (dark) adsorption; (b) the relationship between the extent of adsorption and degradation dynamics; and (c) the dynamics of mineralization (loss of total organic carbon (TOC)). Branching had little, if any impact on the adsorption process by comparison with analogous linear acids reported earlier. Complete degradation of the branched acids occurred in relatively short time ($\leq$2 h), whereas mineralization required longer irradiation times (3–4.5 h). The trends correlate with C–H bond strengths. Branched acids degrade at rates slightly greater than unbranched acids with degradation dynamics decreasing with increase in chain length. The 2-HVA and 2-KVA acids degraded at nearly identical rates. Methylation of 2-HBA had no effect on the dynamics of degradation. However, oxidized carboxylic acids (2-HVA and 2-KVA) degraded five-fold faster than the corresponding linear valeric acid; similarly for 2-OH-2-MBA, which degraded four-fold faster than 2-MBA. These observations explain the difficulty in detecting primary hydroxylated intermediates in $^{\bullet}$OH-radical oxidized linear carboxylic acids.

Keywords: Photodegradation; Photomineralization; Branched carboxylic acids; Oxidized carboxylic acids

1. Introduction

Heterogeneous photocatalysis mediated by UV-irradiated TiO_2 dispersions in aquatic or humidified media is one of several advanced oxidation technologies (AOTs) that are driven largely by the desire to remediate/detoxify polluted ecosystems (atmospheric and aquatic). The process rests mostly with the photogeneration of charged carriers (electron and holes) in their respective conduction and valence bands of the semiconductor photocatalyst, followed by their migration and ultimate trapping at the metal-oxide particle surface where they are poised to undergo redox reactions with suitably adsorbed species. The photonic energy that drives the photophysics and the photochemistry is not without loss because of the inherent recombination of the two charge carriers, either as free or as trapped species [1]. Numerous reports have pointed to the surface-trapped hole (i.e., the surface-bound $^{\bullet}$OH radicals [2]) as the major oxidative entity in the photocatalytic oxidation of a varied class of organic substrates [3].

Aliphatic carboxylic acids perform a diverse range of industrial functions. Some of these acids occur naturally and serve an important function in nutrition (e.g. acetic acid),

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whereas others are intermediate species in normal biochemical processes [4]. The level of industrial production of some of these acids attests to their commercial and industrial significance. Some short chain aliphatic acids can cause acute adverse effects to skin, eyes, and mucous membranes [4]. As well, aliphatic acids interact with cytochrome P450 to produce a metabolite toxic to the liver, while others are teratogenic to laboratory animals [5]. Some aliphatic aldehydes and dicarboxylic acids show carcinogenic activity to some female rodents [6]. The anticonvulsant 2-propylpentanoic acid is teratogenic in humans and rodents [7], whereas octanoic acid is toxic to several insect species [8].

Earlier, we examined [9] linear C1–C5 carboxylic acids and showed that at low catalyst loading (2.0 g/L) and except for formic acid, adsorption of the other four C2–C5 acids increased with chain length, although the overall level was rather small. By contrast, at high catalyst loading all four C2–C5 acids adsorbed to nearly the same extent (15–19%) with adsorption of formic acid on TiO_2 being two-fold greater (34%). The dynamics of degradation and mineralization decreased with increase in chain length; thus, formic acid degraded and mineralized faster than its longer chain congeners. Several intermediates were identified in the degradation of the C3–C5 acids, of which 21 species in the degradation of valeric acid by HPLC co-elution, by gas chromatography (GC–FID) and by gas chromatography coupled to mass spectral detection (GC–MS) techniques. The quantum yields of degradation of the C2–C5 acid series increased with chain length from $\Phi = 0.010$ for acetic acid to $\Phi = 0.067$ for valeric acid; Φ of formic acid was 0.12 ± 0.02 [9].

In the present study, we examined dark adsorption and the dynamics of degradation and mineralization of selected branched carboxylic acids and oxidized carboxylic acids to aid in our understanding of the degradation behavior of the linear C1–C5 aliphatic acid series reported earlier [9].

2. Experimental section

2.1. Chemicals

The commercially available products 2-methylpropanoic acid (2-MPA), 2-methylbutanoic acid (2-MBA), 3-methylbutanoic acid (3-MBA), trimethylacetic acid (TMA), 2-hydroxybutanoic acid (2-HBA), 2-hydroxy-2-methylbutanoic acid (2-OH-2-MBA), 2-ketovaleric acid (2-KVA) sodium salt, and 2-hydroxyvaleric acid (2-HVA) sodium salt hydrate were obtained from Aldrich and were used without further purification. Titanium dioxide, TiO_2, was Degussa P25; its properties are now well established. Other chemicals were of reagent grade quality.

2.2. Irradiation and analyses

Irradiation of the dispersions was achieved using an Oriel 1000 W Hg/Xe arc light source. A water circulating cooling/heating system (MGW–Lauda K4R Electronics) provided control of the temperature of the (double jacketed) reactor during irradiation; temperature was kept at $20 \pm 1\,^{\circ}C$. A Pyrex water bath was also positioned between the reactor and the light source to filter out infrared radiation. Air equilibration was achieved by leaving the reactor opened to the atmosphere at all times during irradiation except during dark adsorption determination. The reactor material (silicate glass) excluded wavelengths shorter than 320 nm from the cell, thereby avoiding direct photolysis of the acids being examined.

The degradation of the branched and oxidized aliphatic acids was monitored by HPLC isocratic techniques using a Waters 501 isocratic apparatus consisting of a Waters 501 pump mounted with a 20 μL injection loop, a Waters 441 UV absorbance detector with single wavelength detection (214 nm), a Hewlett Packard HP3396A integrator, and a Supelco Canada Spherisob reversed phase C_8 (5 μm, 250 mm × 4.6 mm) HPLC column. The column was kept at ambient temperature. Total organic carbon (TOC) analyses were performed on a Shimadzu TOC-500 analyzer.

2.3. Dark adsorption measurements

Fifty milliliters (50.0 ml) of a 2×10^{-3} M solution of the aliphatic carboxylic acids (TMA, 2-MBA, 2-MPA, 3-MBA, 2-HVA, 2-KVA, 2-OH-2-MBA) was introduced into a glass container containing 0.100 g of TiO_2 to give a catalyst loading of 2.0 g/L. The glass reactor was stoppered, sonicated for 5 min, and the suspension was subsequently stirred magnetically in the dark for ca. 90 min. The reactor contents were sampled and the aliquots then filtered through 0.22 μm Spartman-3 filters (Teflon membrane, Schleicher & Schuell) into small glass vials, which were capped and the contents stored in the dark for later analyses. All manipulations were performed under dark conditions. Samples were analyzed by HPLC techniques; the mobile phases are described in Table 1.

2.4. Rates of disappearance of branched and oxidized carboxylic acids

Fifty milliliters (50.0 mL) of a 2.0×10^{-3} M solution of the acid {2-MPA, 2-MBA, 3-MBA, TMA, 2-HVA, 2-KVA, 2-OH-2-MBA, and 2-HBA} was added to the reactor containing 2.0 g/L of TiO_2. The mixture was magnetically stirred in the dark for 90 min, after which a 400 μL aliquot was collected and the remaining dispersion was subsequently UV-irradiated, samples from which were collected periodically, frequently at first and then gradually. They were filtered through 0.22 μm filters into small glass vials, capped and subsequently analyzed by the HPLC method. The relevant mobile phases are summarized in Table 1.

Table 1
Mobile phases used for HPLC isocratic analyses for dark adsorption evaluations and for degradations of branched and oxidized acids

H_2O (% v/v)	MeOH (% v/v)	Acids
Mobile phases for dark adsorption		
75	25	2-Ketovaleric, 2-hydroxyvaleric
65	35	2-Methylpropanoic, 2-methylbutanoic, 3-methylbutanoic, 2-hydroxy-2-methylbutanoic, trimethylacetic
Solvent 1	**Solvent 2**	**Acids**
Mobile phases for degradations		
90% v/v H_2O	10% v/v CH_3CN	2-Methylpropanoic
80% v/v H_2O	20% v/v CH_3CN	2-Methylbutanoic, 3-methylbutanoic, trimethylacetic
75% v/v H_2O	25% v/v CH_3OH	2-Hydroxyvaleric, 2-ketovaleric, 2-methyl-2-hydroxybutanoic
90 v/v H_2O	10% v/v CH_3OH	2-Hydroxybutanoic

The pH was adjusted to 3.0 with *o*-phosphoric acid. Flow rate was 1.0 mL/min, temperature of column was ambient.

3. Results and discussion

Several factors can influence the rate of degradation of organic compounds in UV-irradiated and air-equilibrated aqueous dispersions of titanium dioxide. They include but are not limited to the loading of the photocatalyst, the concentrations of solute and oxygen, the extent of adsorption of solute on the TiO_2 particle surface, the pH of the dispersion, the incident light irradiance from a suitable UV light source, and the prevailing temperature (among others). Most factors can be controlled. In the present study, catalyst loading, solute concentration, incident photon flow, and medium temperature remained otherwise constant. No oxidants were added other than O_2 (air) since experiments were carried out under air-equilibrated conditions; concentration of oxygen was ca. 2.4×10^{-4} M [10].

The rates of degradation may be limited by the rate of electron scavenging by oxygen when the concentration of solute is greater than 10^{-3} M and the partial pressure of oxygen P_O^2 is smaller than ca. 0.05 atm [11]. In the current study, the partial pressure of molecular oxygen (P_O^2) was 1 atm and the solute concentration was ca. 10^{-3} M. Hence, the only variables were (i) the pH of the dispersion and (ii) the extent of adsorption of the organic solute on the catalyst surface. The latter is an intrinsic consequence of the system that can be influenced in part by the pH of the TiO_2 dispersion. For instance, the extent of dark adsorption of organic acids may decrease with increasing pH because of electrostatic repulsion between the dissociated form of the acids and the negatively charged TiO_2 surface [12]. The pH of the dispersion was governed by the respective pK_a's of the carboxylic acids examined, and the nature of the photocatalyst surface.

3.1. Branched C4 and C5 carboxylic acids

3.1.1. pH and dark adsorption

The branched acids were examined under experimental conditions otherwise identical to those used for the C1–C5 linear series reported earlier [9]. The extent of (dark) adsorption and pH results for the branched C4 and C5 carboxylic acids series are listed in Table 2. For dark adsorption, the values represent the mean from four data sets for each acid; errors denote one standard deviation. The variance around the mean of the pH data was negligible and is not reported. The rather large spread in the standard deviations in the adsorption data arises because the extent of adsorption of the branched acids tend to be rather low at a catalyst loading of 2.0 g/mL. That is, differences in peak area in the HPLC chromatograms of the samples, before and after exposure to the UV light source, were small and of the same magnitude as the precision of the method (extent of adsorption was ca. 3–5%; the method's precision was ca. 2%).

The pH of the suspensions containing the four-branched acids was otherwise identical, as expected from the pK_a of the acids (4.84, 4.77, and 5.05 for 2-MPA, 3-MBA, and TMA, respectively). The extent of dark adsorption followed a similar trend. Such observations are in keeping with earlier findings [9] insofar as the extent of dark adsorption of aliphatic carboxylic acids on TiO_2 correlates with the extent of electrostatic interactions between the substrate and the metal-oxide photocatalyst surface. The same situation is seen when comparing the branched acids with their corresponding linear analogs, e.g. (1) 2-methylpropanoic acid relative to butanoic acid (two C4 acids), and (2) 2-MBA, 3-MBA, and TMA relative to valeric acid (four C5 acids), as reported in Table 2.

Within experimental error, there is no difference in dark adsorption between the branched acids, and no differences between the C4 isomers, nor between the C5 isomers. The pH of all the acid solutions remained around 3.7–3.8. Branching had little impact, if any, on dark adsorption of C4 and C5 aliphatic carboxylic acids, and consequently played no role in the adsorption process.

3.1.2. The degradation process

All branched C4 and C5 carboxylic acids examined degraded completely within ca. 1.5 h for 2-methylpropanoic acid and 2 h of irradiation for the other three-branched acid congeners. Accordingly, TiO_2 heterogeneous photocatalysis is appropriate to dispose of branched carboxylic acids from aquatic media.

Degradation of the branched acids yielded intermediate species. Except for TMA, which showed no HPLC evidence

Table 2
Rate data for the degradation and mineralization (loss of TOC) of the branched carboxylic acid series

Acid	pH	% Dark adsorption	Rate of degradation (μmol/h)	Rate of TOC decay (μmol /h)
2-Methylpropanoic	3.7	3.7 ± 1.0	86 ± 5 (89 ± 8)[b]	31.9 ± 1.5 (34.6 ± 0.3)[b]
2-Methylbutanoic	3.8	1.4 ± 2.9 (2.9 ± 2.9)[b]	72 ± 5	26.3 ± 0.3
3-Methylbutanoic	3.7	3.5 ± 1.1	63 ± 2	23.2 ± 0.5
Trimethylacetic	3.8	4.2 ± 2.2 (5.2 ± 2.1)[b]	41 ± 2	26.7 ± 3.3
Butanoic[a]	3.7	3.1 ± 1.0	55 ± 2	25.4 ± 0.2
Valeric[a]	3.8	4.6 ± 1.4	42 ± 2 (45 ± 4)	21.7 ± 0.5

[a] Ref. [9].

[b] Obtained at two different times.

of intermediates remaining in solution once degraded, some intermediates were still present for the other three 2-MPA, 2-MBA and 3-MBA acids under complete degradation conditions. The intermediates eluted at lower retention times than the parent acid, indicating that (1) they contained less carbon atoms, and/or (2) they were hydroxylated or keto acidic species.

For 2-methlypropanoic acid, the preferential site of H-atom abstraction by $^{\bullet}$OH radicals, photogenerated on UV-irradiation of TiO_2, is the hydrogen on the α-carbon $\{CH_3CH(CH_3)COOH\}$. Not only does this acid bear an α-hydrogen atom, but the H atom is also bonded to a tertiary carbon atom, making the C–H bond a somewhat weaker bond relative to secondary and primary carbons. In this regard, molecular orbital calculations of bond lengths and C–H bond dissociation energies using the MOPAC package [9] gave for the C–H bonds at carbons adjacent to the –COOH function (i.e., the α-carbon) the following bond lengths and $\Delta H^{\circ}_{\mathrm{diss}}$: 1.128 A and 124.7 kcal/mol for 2-MPA, 1.090 A and 130.5 kcal/mol for 2-MBA, 1.090 A and 132.1 kcal/mol for 3-MBA, and 1.090 A and 134.9 kcal/mol for valeric acid (VA).

The more stable C-centered tertiary alkyl radical generated $\{CH_3C^{\bullet}(CH_3)COOH\}$ is further resonance-stabilized by the presence of the vicinal carboxyl group [13] and can yield an α-hydroxycarboxylic acid $\{CH_3C(OH)(CH_3)COOH\}$. Such intermediate will likely have a lower retention time in the HPLC chromatogram than its parent compound because addition of a hydroxyl group increases water solubility, thereby reducing its affinity for the stationary phase of the HPLC C_8 column. It should be noted that at the HPLC detection wavelength of 214 nm, it is unlikely that the carboxylic group had been removed at this stage since the signature of the intermediate was still observable. The same rationale applies to 2-methyl and 3-methyl-butanoic acid (and other acids as well), in accord with the mechanism proposed by Sakata and coworkers [14].

3.1.3. *Dynamics of the degradation process*

The temporal course of the degradation of branched carboxylic acid series [9] is illustrated in Fig. 1a and d. A trend similar to that observed for the linear series was obtained whereby the concentration of acid decreased linearly with irradiation time to ultimately depart from linearity at the lower concentrations. Except for 2-MPA, for which the temporal

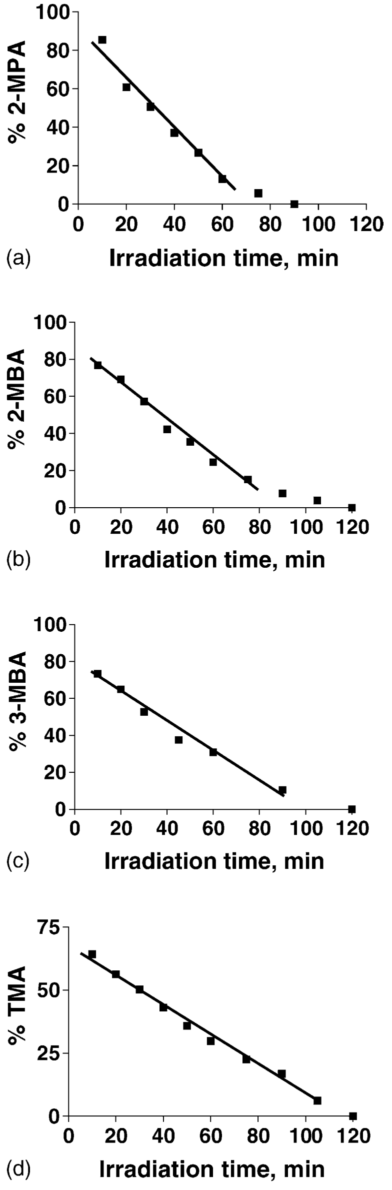

Fig. 1. Temporal course of the degradation of C4 and C5 branched carboxylic acids in UV-irradiated air-equilibrated aqueous dispersions of TiO_2 displayed as percent acid vs. irradiation time: (a) 2-methylpropanoic acid, 2-MPA; (b) 2-methylbutanoic acid, 2-MBA; (c) 3-methylbutanoic acid, 3-MBA; and (d) trimethylacetic acid, TMA. Initial concentration of acids, 2.0×10^{-3} M (=100%), volume, 50 mL.

decrease in concentration remained linear for ca 60 min, time at which ∼10–12% of the acid was still in solution, linearity was maintained for over 70 min for the other three acids, time at which ca. 10% of the initial acid concentration also remained in solutions of the 2-MBA, 3-MBA and TMA acids. The initial zero-order rates of disappearance of these acids are summarized in Table 2.

The rate data reveal that the order of degradation followed the trend: 2-MPA > 2-MBA > 3-MBA > TMA. The pH of a solution and the degree of adsorption of an acid on TiO_2 are intrinsically related and are noted to play a role in the heterogeneous photocatalytic degradation of organic compounds.

As with the corresponding linear analogs [9], the branched acids also tend to be poorly adsorbed. Nonetheless, the extent of dark adsorption was slightly greater for trimethylacetic acid (ca. 4–5%; Table 2). The levels of dark adsorption are not significantly different, however, considering the associated experimental errors. By contrast, the rates are different although the differences are small. Consequently, factors other than dark adsorption must play a role in the observed trend. These may be, for example, (1) the C–H bond strengths, and (2) the pH-dependent oxidative power of the TiO_2 semiconductor. Of the four-branched acids, TMA lacks a secondary or tertiary C–H bond, unlike the 2-MPA, 2-MBA and 3-MBA acids, which all bear tertiary C–H bonds. The lower bond strengths (i.e., $\Delta H^{\circ}_{\text{diss}}$) of these tertiary C–H bonds should contribute positively on the rates of degradation.

Loss of a primary C–H bond by TMA following $^{\bullet}OH$ radical attack on the methyl groups yields a primary alkyl radical intermediate that is less stable than tertiary alkyl radicals produced by the other three acids [13]. On this basis, trimethylacetic acid should be slowest to degrade of the four-branched acids, as observed in Table 2. Hence, the lower rate for TMA is, in part, attributed to the C–H bond strength. Even though faster to degrade than TMA, the rates of degradation of 2-MPA, 2-MBA and 3-MBA display small but finite differences. All three acids bear a tertiary C–H bond (at the branching carbon) and two of these acids (2-MPA and 2-MBA) have their tertiary C–H bond at the α-carbon where the hydrogen is somewhat more labile. If H-atom abstraction by an $^{\bullet}OH$ radical is a significant step in the degradation pathway of these acids, then 2-MPA and 2-MBA should degrade faster, as confirmed in Table 2, since the favored site for $^{\bullet}OH$ radical attack is directed at the hydrogen located on the α-carbon.

As far as the pH-dependent oxidative power of TiO_2 is concerned, since the flat band potentials of the bands shift to more reducing potentials with increase of pH (hence TiO_2 becoming a poorer oxidant) the near identical pHs of the suspensions of the branched acids (Table 2) precludes inferences on the merits of pH variations on the relative rates of degradation. Thus, the observed trend in the rate data of these acids must be attributed but not limited to the relative C–H bond strengths. Nonetheless, the pH factor cannot be dismissed entirely, since pH affects the surface potential of the TiO_2 particle [15] which in turn bears on the overall redox events taking place on the particle surface. The influence of the pH factor was clearly evidenced in the heterogeneous photocatalytic treatment of wastewaters containing metallic contaminants. In most cases, the rate of metal deposition relative to another could be predicted from the respective potentials of the redox couples, E° [16].

3.1.4. *Dynamics of mineralization of branched acids*

The temporal decrease of total organic carbon left in solution was also measured for the branched series. TOC content decreased with irradiation time indicating the complete mineralization of the four-branched acids into water and carbon dioxide. The residual amounts of TOC were statistically negligible for 2-MPA, 2-MBA and 3-MBA acids, unlike TMA, which showed a significant quantity of TOC (ca. 9 mg/L; initial TOC concentration, ca. 100 mg/L) remaining even after 270 min of irradiation.

The dynamics of TOC disappearance for the branched acids are reported in the temporal evolution of the decay of TOC summarized in Fig. 2a–d. As noted earlier for the linear C1–C5 acid series [9], mineralization of the branched acids also followed zero-order kinetics. The relevant rate data of TOC decay are summarized in Table 2.

The overall trend in the rates of TOC disappearance differs from the one obtained for the rates of acid degradation consistent with the earlier trend noted for the linear carboxylic acid series [9]. Although the trend of rates of degradation of branched acids varied as 2-MPA > 2-MBA > 3-MBA > TMA, the corresponding rates of TOC decay were statistically similar within experimental error as shown in Table 2 and Fig. 3; the latter compares rates of degradation with rates of TOC decay in equivalent units (% acid degraded/min and % TOC decayed/min).

The rates of TOC decay of all four branched acids are lower than the rates of degradation owing to the accumulation of carbon-containing refractory intermediates or, alternatively, intermediates that competed with the parent compounds for the same surface-active sites of the photocatalyst. Fig. 4 validates this notion further. In the first 90 min of irradiation, the gap between the quantity of 3-methylbutanoic acid remaining and the mass balance (i.e., % acid degraded plus % TOC degraded) increased while concomitantly this balance deviated negatively from 100%. Clearly, TOC analysis is the method to evaluate the degree of removal of total contaminants from an aquatic medium.

Returning to the possible impact of branching on the rates of degradation of this class of compounds, we recall that observed trends were based principally on C–H bond strengths. If this factor were indeed significant, the rates of degradation of all branched acids ought to be greater than the rates of degradation of their linear analogs. With the exception of trimethylacetic acid, for which the rate of disappearance is comparable to its linear C5 acid analog (Table 2), all branched acids degraded at a faster rate than the corresponding linear analogs. Clearly, branching makes these compounds less refractory to oxidative degradation.

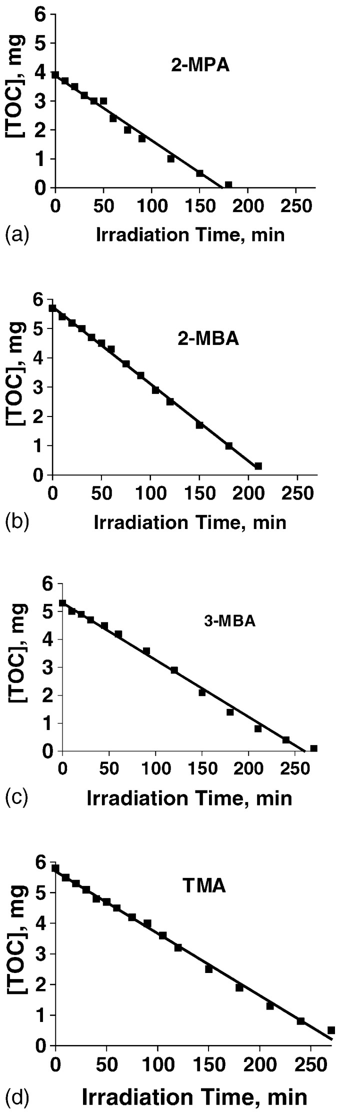

Fig. 2. Temporal course of the decay of total organic carbon (TOC) of C4 and C5 branched carboxylic acids in UV-irradiated air-equilibrated aqueous dispersions of TiO_2 displayed as miligram of TOC vs. irradiation time: (a) 2-methylpropanoic acid, 2-MPA; (b) 2-methylbutanoic acid, 2-MBA; (c) 3-methylbutanoic acid, 3-MBA; and (d) trimethylacetic acid, TMA. Initial concentration of acids, 2.0×10^{-3} M; volume, 50 mL; initial concentration of TOC, around 100 ppm (mg/L).

3.1.5. Attempts to identify oxidized intermediates by HPLC co-elution

Selected acids were examined for the presence of oxidized intermediates by the HPLC co-elution method. The investigation was also carried out to ascertain whether acids other than α-hydroxy and/or α-keto compounds were produced so as to gain further insights of the intermediates formed during the photocatalytic degradation of the branched acids. Preliminary experiments suggested that 5 h of irradiation of the air-equilibrated aqueous TiO_2 suspension containing 2-methylpropanoic acid sufficed to produce a reasonable quantity of intermediates for use of the co-elution method. In the case of 2-methylbutanoic acid, 8 h of irradiation were required. The HPLC co-elution method was described earlier [9]. In the present instance, the irradiated suspension of TiO_2/2-MPA was spiked with a pure sample of 2-hydroxy-2-methylpropanoic acid (2-OH-2-MPA); the TiO_2 dispersion containing 2-MBA was spiked with a sample of 2-OH-2-MBA.

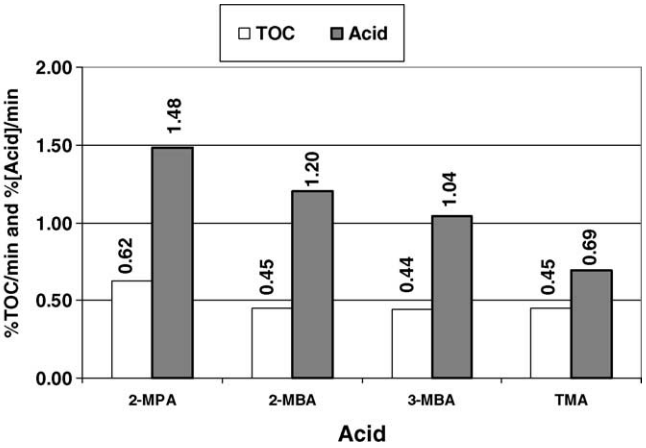

Fig. 3. Histogram displaying a comparison of the rates of TOC decay (as %/min) against the rates of degradation of the branched C4 and C5 carboxylic acids (also as %/min).

Neither of the two potential intermediates was detected by the co-elution method, although their formation is not precluded since the rates of degradation of α-hydroxy and α-keto carboxylic acids are about five-fold faster than the parent substrates (see below) [9]. This is consistent with previous studies by Minero and co-workers [17], who reported that dodecyl derivatives (1-dodecanol and dodecanoic acid) degraded at rates a hundred-fold faster than dodecane, and that CO_2 evolved almost at the same rate at which dodecane degraded. Such observations inferred low steady-state concentrations of oxygenated intermediates. Others reported that the first step in the degradation of acetic acid on suspended

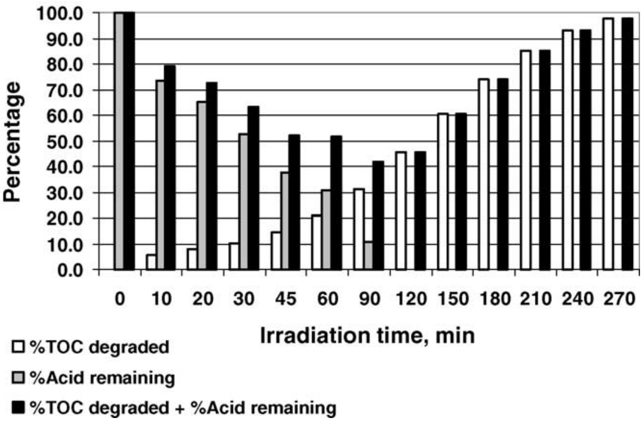

Fig. 4. Histograms depicting the temporal behaviour of the rates of TOC decay (as %/min); rates of acid degradation (as %/min); and the mass balance as % TOC degraded plus % acid degraded for the C5 branched carboxylic acid; 3-methylbutanoic acid (3-MBA).

TiO_2 particles involved formation of surface-bound $^\bullet OH$ radicals through hole trapping, and that $^\bullet OH$ radical abstraction of the α-hydrogen on the acid molecule yielded glycolate ($HOCH_2COO^-$) and glyoxylate ($OCHCOO^-$) species [18]. By contrast, heterogeneous photocatalytic studies involving organic acids in aqueous media, and more specifically acetic acid, propanoic acid and butanoic acid, showed no formation of α-hydroxy acids or α-keto compounds [14]. Rather, aldehydes, ketones and alcohols were identified along with other carboxylic acids having more or less carbon atoms (different chain lengths). However, our recent study involving the photocatalytic method identified 2-hydroxybutanoic acid in the degradation of valeric acid, thereby confirming hydroxylation of the α-carbon of the aliphatic carboxylic acids [9].

3.2. Alpha-hydroxy and alpha-keto C5 aliphatic carboxylic acids

3.2.1. pH and dark adsorption

The α-hydroxy and α-keto acids {2-hydroxy-2-methylbutanoic acid (2-OH-2-MBA), 2-hydroxyvaleric acid (2-HVA), and 2-ketovaleric acid (2-KVA)} were investigated because they represented potential intermediates among many formed during the degradation of linear and branched carboxylic acids. Experimental conditions used were otherwise identical to those used for the linear [9] and branched series (see above). The parameter not controlled in the experiments was the pH of the solution/dispersion, governed entirely by the nature of the carboxylic acid and the photocatalyst surface. Table 3 summarizes the variations in adsorption behavior and pH obtained for the three α-hydroxy/keto acids. The greater the pH, the lesser the extent of adsorption.

The pHs of the TiO_2 suspensions of 2-HVA and 2-KVA acids were greater (pH = 6.1 and 6.5, respectively) than the pH of the corresponding suspension containing the non-oxidized parent substrate (valeric acid; pH = 3.8). There is an inverse relationship between pH of the suspensions and the level of dark adsorption of these acids. We also hasten to note that variations in adsorption are not caused by (1) adsorption of the acid on the walls of the reactor, (2) nor onto the membrane filters used to filter the samples prior to HPLC analysis, nor to (3) degradation of the acids in the filtrate during sample manipulation.

Similar to the linear and branched series, this trend is in keeping with the extent of dark adsorption of aliphatic carboxylic acids on TiO_2 caused by electrostatic interactions between the dissociated acids and the positively charged TiO_2 particles whose surface is neutral at ca. pH = 5.5–6.0 (=pzc [11]). Comparison of pH and dark adsorption data for the non-oxidized acid, the α-hydroxy acid and α-keto acids (Table 3) also shows this inverse relationship. For instance, the pH of the suspensions containing valeric acid, 2-hydroxyvaleric acid, and 2-ketovaleric acids were 3.8, 6.1 and 6.5, respectively, whereas the degree of dark adsorption was, respectively, 4.6, 2.2, and 1.4%. Similarly, for 2-MBA and 2-OH-2-MBA; the pH of their suspensions was 3.8 and 3.3, respectively (see Tables 2 and 3). The related dark adsorption levels were 2.9 and 5.5%, respectively. Accordingly, we deduce that the dominant factor impacting on dark adsorption is the pH of the suspensions in these cases.

3.2.2. Extent of degradation

Of the available oxidized acids, 2-oxovaleric acid and 2-hydroxy-2-methybutanoic acid were chosen for further study. Our primary interest in their degradation was to examine the dynamics of the degradative process. The two acids underwent complete or nearly complete degradation under our conditions. No peak of the 2-oxovaleric acid was seen after 44 min of irradiation in the HPLC chromatograms. A very small peak was still present after 20 min of irradiation for the 2-OH-2-MBA. These acids degraded much faster than their non-oxidized straight chain analogs. Since, the latter were demonstrated to be fully mineralized when exposed to UV-irradiation in the presence of TiO_2 specimens [9], we deduce that these oxidized acids are also fully mineralized when subjected to the same oxidation methods.

The HPLC chromatograms recorded during the degradation of 2-oxovaleric acid and 2-hydroxy-2-methylbutanoic acid also showed that most, if not all, of the detectable intermediates eluted at longer times than the parent acids. In a related experiment, degradation of 2-hydroxyvaleric acid and 2-hydroxybutanoic acid revealed intermediates with peaks at shorter retention times than the parent acids, in addition to a peak at a longer retention time. No attempts were made to

Table 3
First-order kinetics and initial zero-order rate data for the degradation of α-hydroxy and α-keto carboxylic acids together with the two C4 and C5 linear acids reported for comparison

Acid	pH	% Dark adsorption	k (min^{-1})	Rate of degradation (μmol/h)
2-Hydroxybutanoic	–	3.7 ± 0.0	0.076 ± 0.004	289 ± 7
2-Hydroxyvaleric	6.1	2.2 ± 0.4	0.059 ± 0.003	214 ± 22
2-Ketovaleric	6.5	1.4 ± 0.2	0.062 ± 0.003	215 ± 21
2-Hydroxy-2-methylbutanoic	3.3	5.5 ± 0.2	–	280 ± 24
	3.7		–	
Butanoic[a]	3.7	3.1 ± 1.0	–	55 ± 2
Valeric[a]	3.8	4.6 ± 1.4	–	42 ± 2 (45 ± 4)

[a] Ref. [9].

identify the intermediates, though we suspect they may be dehydrated forms of the starting material (e.g., 2-butenoic acid from 2-hydroxybutanoic acid). The absence of the hydroxyl group would explain the longer retention time, since 2-butenoic acid is less water-soluble than 2-hydroxybutanoic acid.

That most (if not all) of the intermediates from 2-oxovaleric acid and 2-hydroxy-2-methylbutanoic acid degradation eluted at longer retention times than the parent acids indicates that these intermediates have more affinity for the stationary phase (reverse-phase C8), and thus are less water-soluble than the starting materials. Many compounds meet this simple requirement, e.g., aldehydes of approximately the same chain length, lower molecular weight non-oxidized carboxylic acids, unsaturated carboxylic acids, alkenes, and alcohols among several others. For instance, butanal ($CH_3CH_2CH_2CHO$) and butanoic acid ($CH_3CH_2CH_2CO_2H$) may form from decarboxylation of 2-oxovaleric acid, and although these C4 species have one carbon atom less than 2-oxovaleric acid, it should not cause them to elute at shorter retention times since the 2-keto and 2-hydroxy compounds eluted at shorter retention times than non-oxidized acids of lower molecular weight, with the keto compounds eluting first. As an example, we note that the retention time of butanoic acid was longer than that of 2-hydroxy and 2-keto C5 acids when eluted under the same chromatographic conditions.

3.2.3. *Dynamics of the degradation process*

The temporal course of the degradation of 2-hydroxybutanoic acid (2-HBA), 2-hydroxyvaleric acid (2-HVA), 2-oxovaleric acid (2-KVA) and 2-hydroxy-2-methylbutanoic acid (2-OH-2-MBA) is illustrated in Fig. 5a to d. Except for the latter hydroxy acid, the trend is in contrast to that observed for the linear acid series [9] and for the branched series (see above). The initial acid concentration (2.0×10^{-3} M) decreased exponentially with irradiation time through first-order kinetics. It is evident that these oxidized acids degraded faster than the corresponding non-oxidized linear and branched acids.

The first-order kinetics and the initial (zero-order) rates of degradation of these acids are summarized in Table 3 along with those of the corresponding linear C4 and C5 acids for comparison [9]. Under otherwise identical conditions, the initial rates of degradation were greater for 2-hydroxybutanoic acid (289 μmol/h) and 2-hydroxy-2-methylbutanoic acid (280 μmol/h), whereas the α-hydroxy and α-oxovaleric acids degraded more slowly (214 and 215 μmol/h, respectively), but nonetheless faster than their parent linear acids. As noted for the linear C1–C5 linear acids [9] and for the branched C4/C5 series, the pH of the dispersions and degree of adsorption of the acid on TiO_2 played a non-insignificant role in the heterogeneous photocatalytic degradation of these substrates. This influence is evidenced on comparing dark adsorption data of the acids with their respective rates of degradation (Table 3).

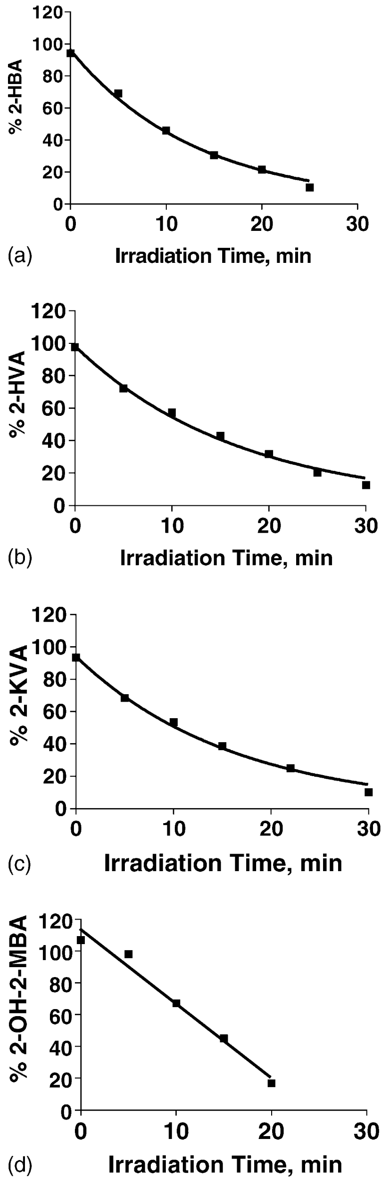

Fig. 5. Plots illustrating the dynamics of degradation of C4 and C5 oxidized forms of the carboxylic acids (as percentage against irradiation time) in UV-irradiated TiO_2 dispersions for: (a) 2-hydroxybutanoic acid, 2-HBA; (b) 2-hydroxyvaleric acid, 2-HVA; (c) 2-oxo(keto)valeric acid, 2-KVA; and (d) 2-hydroxy-2-methylbutanoic acid, 2-OH-2-MBA. Initial concentration of acids, 2.0×10^{-3} M; volume, 50 mL.

Consistent with the linear and branched series, the α-hydroxy and α-keto acids also tend to adsorb poorly on TiO_2 with the highest extent of adsorption seen for 2-hydroxy-2-methylbutanoic acid (5.5%). The adsorption data are significantly different when considering their associated errors. The two acids (2-HBA and 2-OH-2-MBA) that adsorbed the most gave rise to the faster rates of degradation, an observation expected if reactions occur at the surface of the photocatalyst. We should also note that the reaction media of the two acids that gave rise to the lower rates of degradation had the higher pH. For 2-HVA and 2-KVA solutions the pH's were 6.1 and 6.5, respectively, as opposed to pH = 3.3

for the 2-OH-2-MBA acid. The oxidative power of TiO_2 is pH-dependent and becomes more reducing as pH increases. Consequently, the lower rates obtained for 2-hydroxyvaleric acid and 2-ketovaleric acid, relative to the other two acids, can be rationalized in part in terms of the pH of the suspensions since pH impacts on the adsorption characteristics of these acids on the catalyst surface (electrostatic attraction) and on the oxidative power of the photocatalyst.

At pH 6.1 and 6.5, pHs slightly above the isoelectric point of TiO_2 (5.5–6.0) [11], the surface of the photocatalyst is slightly negative and of the same charge as the carboxylate salts, a situation that does not favor adsorption of these anions. Concomitantly, the oxidative power of TiO_2 under such conditions is smaller. These two factors contributed to the lower rates of degradation of 2-HVA and 2-KVA, as opposed to the 2-HBA and 2-OH-2-MBA acids (Table 3).

Of the acids examined, the experimental observations can be accounted by considering (1) the extent of dark adsorption of the acids on the surface of the photocatalyst, (2) the pH of the suspensions which impacts on adsorption, (3) on the oxidative power of the photocatalyst, and (4) the C–H bond strengths. Taking that all these factors impinge on the dynamics of degradation, they should also explain differences observed across the three series of carboxylic acids (linear, branched and oxidized). The analysis begins with valeric acid, 2-hydroxyvaleric acid and 2-ketovaleric acid (linear versus oxidized).

As expected, the pH of the dispersions of the acids and the dark adsorption levels are inversely related. The pH of the suspension of valeric acid was lower than the isoelectric point of TiO_2. Hence, TiO_2 was positively charged, a situation that contributes to the attraction of negatively charged, dissociated valeric acid to the metal-oxide surface. At the other extreme, 2-ketovaleric acid gave rise to the lowest level of dark adsorption on TiO_2; its pH was the highest of the three acids. Despite the greater extent of dark adsorption and the low pH, two factors that contribute to a faster rate of degradation, yet valeric acid gave rise to the slower rate among the three acids. Possibly, 2-hydroxyvaleric acid bears a more labile H atom on the α-carbon because of the presence of the OH group on that same carbon. However, this is not so for 2-ketovaleric acid, which bears a H-free α-carbon atom.

H-atom abstraction is not a mandatory and unique pathway toward mineralization of these compounds. Carboxylic acids (or more precisely carboxylate anions) can also be decarboxylated through oxidative electron transfer between the R–COO$^-$ function and the surface-bound $^{\bullet}$OH radical Ti^{IV}–$^{\bullet}$OH (i.e., the so-called surface-trapped hole h_{tr}^{+}) to yield a C-centered alkyl radical and ultimately CO_2. The greater relative stability of the alkyl radicals also impacts on the ease at which these reactions proceed to completion (greater driving force, ΔG^o of the reaction). In this regard, the more stabilized the radical intermediate is, the higher the rate will be.

On decarboxylation, valeric acid yields a rather poorly stabilized primary n-butyl radical intermediate. By contrast, both α-hydroxy and α-ketovaleric acid on decarboxylation lead, respectively, to hydroxyalkyl and ketoalkyl radicals, which are resonance-stabilized by the hydroxyl group and the keto group [13]. This can lead to rate enhancements for these two hydroxyl and keto acids as opposed to valeric acid [19]. A similar analysis holds between 2-methylbutanoic acid and its α-hydroxylated form 2-OH-2-MBA (see Tables 2 and 3). An inverse relationship between dark adsorption and pH is again evidenced. However, as expected and contrary to the data above the trend in the rates of degradation shows a higher rate of degradation for the acid most adsorbed on TiO_2 (dark), and for which the pH of the dispersion was lowest. Nevertheless, although (1) suspensions of both acids have a similar pH, (2) the extent of dark adsorption on the catalyst surface differs by a factor of ca. two, and (3) the 2-hydroxy-2-methylbutanoic acid bears no H-atom on the α-carbon, yet 2-OH-2-MBA shows a rate of degradation nearly four-fold greater than that of 2-methylbutanoic acid. This indicates that factors other than pH, extent of dark adsorption and the presence of labile protons impact on the dynamics of the degradative process.

Subsequent to decarboxylation, 2-methylbutanoic acid yields a secondary alkyl radical, whereas 2-hydroxy-2-methylbutanoic acid yields a hydroxyalkyl radical that can be resonance-stabilized by the presence of the OH group bonded to the carbon bearing the lone electron. Accordingly, the relative stability of the radical intermediates that form during the reactions correlate with the observed rates of degradation. Treatment of wastewaters containing metallic pollutants by this heterogeneous AOT method [20] showed that most metals can be extracted by photoelectrodeposition onto a semiconductor suspended in aqueous media in a manner related to the redox potentials E°. In general, the higher the reduction potential the faster was the rate of deposition. A similar argument can be made for organic compounds. That is, the magnitude of the potential of the redox adsorbate couple [21] might be the ultimate factor governing the rates of degradation of the acids.

4. Concluding remarks

Under otherwise identical experimental conditions (catalyst load, 2.0 g/ml; solute concentration, 2.0×10^{-3} M; dark equilibration time, 90 min), dark adsorptions of the four-branched acids on TiO_2 were statistically identical (3.5–5%). Comparison between branched acids and their corresponding linear acids [9] reveals that branching has no impact on the extent of dark adsorption on the metal-oxide surface and thus has little relevance in the adsorption process. The 2-MPA, 2-MBA, 3-MBA and TMA acids were completely degraded and ultimately mineralized (TOC analyses) when exposed to artificial UV light in an aqueous suspension of TiO_2.

The trends observed for the rates of disappearance of the acids followed the relative C–H bond strengths. The rates were faster for those acids with branching that led to tertiary C–H bonds, with the effect more pronounced when branching was located on an α-carbon, thereby increasing the lability of the α-hydrogen. The rates of degradation of the branched acids differed from the rates of TOC decay. No α-hydroxy or α-keto derivatives were detected in the mineralization of 2-methylpropanoic acid and 2-methylbutanoic acid to CO_2 probably because of the rapid degradation of such oxidized intermediates.

Under identical experimental conditions (catalyst load, 2.0 g/mL; solute concentration, 2.0×10^{-3} M; dark equilibration time, 90 min), an inverse correlation between pH and dark adsorption levels was noted for TiO_2 suspensions of 2-OH-2-MBA, 2-HVA, and 2-KVA acids. Also, the extent of dark adsorption of aliphatic α-hydroxy and α-keto carboxylic acids on TiO_2 can also be rationalized on the basis of an electrostatic model. Such acids degrade some 4–5 times faster relative to the corresponding C4 and C5 linear acids.

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