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An Unexplored O_2-Involved Pathway for the Decarboxylation of Saturated Carboxylic Acids by TiO_2 Photocatalysis: An Isotopic Probe Study

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Abstract: The aerobic decarboxylation of saturated carboxylic acids (from C_2 to C_5) in water by TiO_2 photocatalysis was systematically investigated in this work. It was found that the split of C^1–C^2 bond of the acids to release CO_2 proceeds sequentially (that is, a C_5 acid sequentially forms C_4 products, then C_3 and so forth). As a model reaction, the decarboxylation of propionic acid to produce acetic acid was tracked by using isotopic-labeled $H_2{}^{18}O$. As much as ≈42 % of oxygen atoms of the produced acetic acids were from dioxygen ($^{16}O_2$). Through diffuse reflectance FTIR measurements (DRIFTS), we confirmed that an intermediate pyruvic acid was generated prior to the cut-off of the initial carboxyl group; this intermediate was evidenced by the appearance of an absorption peak at 1772 cm^{-1} (attributed to C=O stretch of α-keto group of pyruvic acid) and the shift of this peak to 1726 cm^{-1} when $H_2{}^{16}O$ was replaced by $H_2{}^{18}O$. Consequently, pyruvic acid was chosen as another model molecule to observe how its decarboxylation occurs in $H_2{}^{16}O$ under an atmosphere of $^{18}O_2$. With the α-keto oxygen of pyruvic acid preserved in the carboxyl group of acetic acid, ≈24 % new oxygen atoms of the produced acetic acid were from molecular oxygen at near 100 % conversion of pyruvic acid. The other ≈76 % oxygen atoms were provided by H_2O through hole/OH radical oxidation. In the presence of conduction band electrons, O_2 can independently accomplish such C^1–C^2 bond cleavage of pyruvic acid to generate acetic acid with ≈100 % selectivity, as confirmed by an electrochemical experiment carried out in the dark. More importantly, the ratio of O_2 participation in decarboxylation increased along with the increase of pyruvic acid conversion, indicating the differences between non-substituted acids and α-keto acids. This also suggests that the O_2-dependent decarboxylation competes with hole/OH-radical-promoted decarboxylation and depends on TiO_2 surface defects at which Ti_{4c} sites are available for the simultaneous coordination of substrates and O_2.

Keywords: carboxylic acids · decarboxylation · isotopic labeling · photocatalysis · titanium dioxide

Introduction

As one of the most important methods for the elimination of pollutants, TiO_2 photocatalysis has been extensively studied and widely used in this field for decades.[1–3] Upon UV irradiation, most organic pollutants can be effectively degraded through surface-mediated redox processes performed by photon-excited hole–electron pairs. However, to date, little is known about how the mechanism of the cleavages of old bonds and formation of new bonds for hydrocarbon moieties is tuned by holes, electrons, and subsequent underlying reactants such as O_2 and H_2O in this intricate heterogeneous system. In spite of the complexity of initial organic pollutants in TiO_2-mediated photodegradation processes, carboxylic acids are always observed to accumulate and account for the majority of converted initial substrates besides CO_2.[1,2] Apparently, the formation of these fragment acids and their further decomposition to achieve complete mineralization constitute the most fundamental steps of C–C bond destruction, which has always been believed to directly affect or even sometimes decide the whole fateful efficiency of photocatalytic transformations.[1,2] However, the details of decarboxylation that affords the decomposition of the acids as well as the details of subsequent carboxylation are not entirely clear yet, even in the cases of most simple saturated straight-chain carboxylic acids with less than five carbon atoms.

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Serpone et al. have systematically examined the photocatalytic decarboxylation of saturated straight-chain carboxylic acids in aerated aqueous TiO_2 dispersions, which showed that the degradation intermediates were mainly composed of shorter-chain monocarboxylic acids.[4] Roughly, the decarboxylation can be considered as the split of $C^1{-}C^2$ bond in the substrate acid and simultaneous release of CO_2 [Eq. (1)].

$$-(CH_2)_n-{}^2CH_2-{}^1COOH\xrightarrow[TiO_2/UV]{O_2/H_2O}\text{-}(CH_2)_{n-1}-{}^2CH_2-{}^1COOH+CO_2 \tag{1}$$

The prevalent mechanism for the decarboxylation has been proved that the split of $C^1{-}C^2$ bond exclusively originates from hole oxidation [Eq. (2)],[4–6] in which h^+ is a photogenerated hole in the valence band. Subsequent intermediate products are alkanes formed under deaerated conditions by means of so-called photo-Kolbe reactions [Eqs. (2) and (3)][5] (e^-_{cb} is a photogenerated electron in the conduction band). Such phenomena have also been observed in the thermal oxidative decarboxylation of these acids by high-valence metal ions, such as Co^{III},[7] Pb^{IV},[8] and Mn^{III},[9] although the main decarboxylation products were alkenes rather than alkanes since no reductive species [like the electrons shown in Eq. (3)] were involved. When O_2 is present, it will react with the generated carbon-centered radicals to finally form hydroxylated and carbonylated intermediates (i.e., -ols/ones)[6] obeying the Russell mechanism for the decomposition of peroxyl radicals via quaternion-peroxide intermediates[10] [Eqs. (4)–(7)].

$$RCH_2COO^-\xrightarrow[-CO_2]{+h^+}RCH_2^{\bullet} \tag{2}$$

$$\begin{aligned}&RCH_2^{\bullet}+e^-_{cb}+H^+\rightarrow RCH_3\\&RCH_2^{\bullet}+RCH_2^{\bullet}\rightarrow RCH_2{-}CH_2R\end{aligned} \tag{3}$$

$$RCH_2^{\bullet}+O_2\rightarrow RCH_2OO^{\bullet} \tag{4}$$

$$O_2+e^-_{cb}+H^+\rightarrow {}^{\bullet}OOH \tag{5}$$

$$RCH_2OO^{\bullet}+{}^{\bullet}OOH\rightarrow RCH_2OOOOH \tag{6}$$

$$\begin{aligned}RCH_2OOOOH+RCH_2COOH\rightarrow &RCH_2OH+RCHO+\\&O_2+CO_2\end{aligned} \tag{7}$$

OH radicals are also regarded to be important oxidative species that act as "diffusive holes" in this decarboxylation process.[11] Moreover, O_2 may be reduced by photogenerated electrons to form H_2O_2, which could be further transformed into OH radicals to promote decarboxylation, although this conversion, which is restricted by several integral steps, should only provide a minor contribution to the decarboxylation process.[2] In the alleged universal mechanism argument, the direct release of CO_2 arbitrarily attributed to hole/OH radical oxidation as well as the involvement of O_2 through free-radical reactions has been the key point. However, the established mechanism is not completely consistent with the experimental observations: 1) although -ols and -ones are relatively stable under most oxidative conditions,[12] it is always shorter-chain acids rather than -ols/ones that are detected as the main intermediates with bare TiO_2 as photocatalyst;[4] 2) even if sometimes -ols and -ones are too unstable to attain observable concentration in the reactions, holes/OH radicals cannot oxidize them to produce acids without O_2, for example, it is acetone rather than pyruvic acid or acetic acid as the final product in the oxidation of isopropanol promoted only by holes/OH radicals in the absence of O_2.[13] This means that there are other possible unexplored O_2-involved pathways for the decarboxylation of carboxylic acids by TiO_2 photocatalysis.

In this work, detailed ^{18}O-isotopic-labeling experiments (with $H_2{}^{18}O$ and $^{18}O_2$) were carried out to investigate the decarboxylation of saturated straight-chain carboxylic acids by TiO_2 photocatalysis (unless specially indicated, an anatase TiO_2 film supported on a glass plate was used). Through analyzing the distribution of isotopic-labeled oxygen atoms from O_2 or H_2O in product acids along with the conversion of substrate acids, we will accurately show the relative contribution of O_2 to the decarboxylation process. We also employed diffuse reflectance FTIR measurements (DRIFTS)[14] combined with ^{18}O-isotopic-labeling method to identify important intermediates in the decarboxylation process. Meanwhile, well-defined electrochemical experiments[15] were performed for the observation of the influence of electrons and O_2 on focused decarboxylation reactions without the involvement of holes/OH radicals. Through performing these detailed investigations, we expect that some results of this research can be useful in understanding the intrinsic role of O_2 as well as clarifying the mechanisms of decarboxylation in TiO_2 photocatalytic reactions.

Results and Discussion

To gain more understanding of the decarboxylation process in the presence of O_2, first of all we re-examined the degradation of some saturated straight-chain carboxylic acids (from acetic acid to valeric acid) in aerated aqueous solutions by TiO_2 photocatalysis. The temporal concentration changes of substrate acids and generated intermediates in the reactions were measured by ion chromatography (IC; Figure S1 in the Supporting Information). Table 1 lists the main generated intermediates and their highest yields during the degradation of the acids. Note that formic acid was detected as an intermediate in the degradation of every acid, but the yield of it was only determined in the degradation of acetic acid due to its very low concentration and the peak overlap between it and propionic acid in IC when investigating the degradation of other acids. Moreover, we calculated the total organic carbon (TOC) values of the remaining substrates and generated intermediates at different time intervals during the degradation of the acids according to the IC results and compared them with those of the

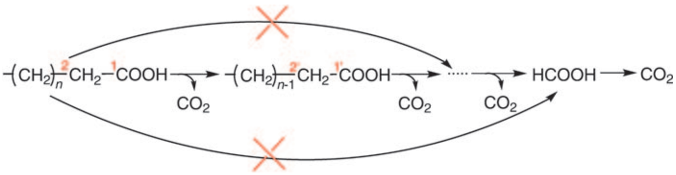
Table 1. The main generated intermediates and their highest yields during the degradation of C_2–C_5 acids by TiO_2 photocatalysis as well as the proportion of calculated TOC to measured TOC at the time point of 2 h UV irradiation in the degradation of the acids.

Substrate[a]	Intermediates	Yields[b] [%]	P[c] [%]
CH_3COOH	$HCOOH$	1.3	99.1
C_2H_5COOH	CH_3COOH	31.5	97.6
n-C_3H_7COOH	CH_3COOH	17.3	98.5
	C_2H_5COOH	21.0	
n-C_4H_9COOH	CH_3COOH	13.6	95.1
	C_2H_5COOH	7.0	
	n-C_3H_7COOH	1.1	

[a] Experimental conditions: solution of acid in water (30 mL, 2 mM) in a 50 mL vessel. [b] The highest yield of this intermediate during the degradation of the substrate acid, which was calculated according to yield = (highest intermediate concentration)/(initial substrate concentration). [c] P = calculated TOC/measured TOC, which was based on the IC and TOC data obtained at the time point of 2 h UV irradiation.

whole solutions measured by a TOC analyzer (Figure S2 in the Supporting Information). The proportions of calculated TOC to measured TOC at the time point of 2 h UV irradiation are also listed in Table 1.

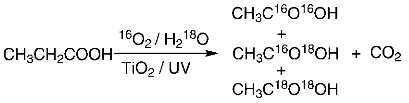
The less than 5% differences between the calculated TOC values and the measured ones confirmed that the detected, linear, non-substituted, shorter-chain monocarboxylic acids constituted the main degradation intermediates. Moreover, regardless of the initial substrate acids (from C_2 to C_5), 1) these shorter-chain acid intermediates remained in the solution and almost accounted for the total conversion of initial substrate besides CO_2; 2) nearly all the presumable inferior acids ($n-1$, $n-2$, ...) originating from the parent acid, even C_1 formic acid, steadily appeared without exception and could be quantified, although their features of accumulation to attain the highest concentrations differed; 3) acetic acid was always generated and significantly accumulated during the degradation of all longer-chain acid substrates. These results, highly similar to those of Serpone's previous work,[4] draw the outline for the degradation and decarboxylation of a carboxylic acid by TiO_2 photocatalysis (Scheme 1): the C^1–C^2 bond split of the acids is invariably sequential (i.e., a C_5 acid sequentially forms C_4 products, then C_3 and so forth) until formic acid was generated; no diacids or -ols/ones as obligatory intermediates were detected as described in the mechanism given in Equations (2)–(7). This strongly suggests the fact that decarboxylation is to simultaneously break the old C^1–C^2 bond of substrate acid and establish new carboxyl group of the inferior acid. Moreover, there must be some intermediates prior to the cleavage of C^1–C^2 bond and release of CO_2, otherwise, we can only observe the direct generation of CO_2 rather than the accumulation of every shorter-chain acid.[16] Following the above notions, we chose propionic acid as the model substrate, because its main decarboxylation product, acetic acid, was stable enough to achieve very high accumulation concentration for ready analysis, to specifically search for the most suitable precursor for the CO_2 departure and clarify the role of O_2 in designed TiO_2 photocatalytic experiments.



Scheme 1. One-by-one cleavages of C^1–C^2 bonds in carboxylic acids.

Since the oxidative decarboxylation and subsequent formation of new carboxyl group promoted by holes and OH radicals requires H_2O participation regardless of hydrolysis or addition reactions, we performed an isotopic labeling experiment using $H_2{}^{18}O$ (96%) to observe the ^{18}O profile of the produced acetic acid in the aerobic decarboxylation of propionic acid by TiO_2 under UV irradiation (Table 2). This way, the O_2 entrance into product acids can be also revealed. Since the formed acetic acid as intermediate could also be further degraded, its steady concentration just accounted for about 0.2 equiv of the converted propionic acid. Blank experiments were performed to examine the oxygen exchange between the carboxyl groups of these acids (acetic and propionic acid) and $H_2{}^{18}O$ and showed that such exchange was negligible (Table S1 in the Supporting Information), which ensured the credibility of our isotopic labeling experiments. Table 2 shows the results of the experiments at 25.1 and 55.6% conversion of propionic acid. Although the concentration of dissolved $^{16}O_2$ was much lower than that of $H_2{}^{18}O$, quite impressive ^{16}O abundance was detected in the acetic acid product. As high as ≈42% of oxygen atoms in the acetic acid were exclusively from $^{16}O_2$ at 25.1% conversion of propionic acid (Table 2, entry 1). Besides the generation of anticipated $CH_3C^{18}O^{18}OH$, $CH_3C^{16}O^{16}OH$ and $CH_3C^{16}O^{18}OH$ were also generated, distinctly indicating that O_2 can accomplish the formation of the new carboxyl group in product acid either by itself or via a possible concerted

Table 2. The decarboxylation of C_2H_5COOH by TiO_2 photocatalysis in $H_2{}^{18}O$ and the isotopic distribution of produced CH_3COOH.[a]



$$CH_3CH_2COOH \xrightarrow[TiO_2\,/\,UV]{^{16}O_2\,/\,H_2{}^{18}O} \begin{matrix} CH_3C^{16}O^{16}OH \\ + \\ CH_3C^{16}O^{18}OH \\ + \\ CH_3C^{18}O^{18}OH \end{matrix} + CO_2$$

	Conversion[b] [%]	Yield[c] [%]	Percentage of various CH_3COOH isotopomers[d] [%]				
			$^{16}O^{16}O$	$^{16}O^{18}O$	$^{18}O^{18}O$	^{16}O[e]	^{18}O[e]
1	25.1	20.0	23.0	38.9	38.1	42.5	57.5
2	55.6	16.2	14.5	33.9	51.6	31.5	68.5

[a] Experimental conditions: solution of C_2H_5COOH in $H_2{}^{18}O$ (1.5 mL, 20 mM) in a 10 mL vessel. [b] The conversion of propionic acid. [c] The fractional yield of acetic acid, which was calculated according to yield = c (generated acetic acid)/c (converted propionic acid). [d] Calculated by the integration of corresponding peak area obtained from mass spectrometry. [e] The total proportion of ^{16}O or ^{18}O in the carboxyl group of CH_3COOH, which was calculated according to $^{16}O = {}^{16}O^{16}O + {}^{16}O^{18}O/2$, $^{18}O = {}^{18}O^{18}O + {}^{16}O^{18}O/2$.

reaction. At higher conversion of 55.6 %, the ratio of O_2 participation to H_2O participation decreased, indicating that decarboxylation of the saturated acid is a quite complex process for the involvement of both O_2 and H_2O. To clarify in which steps O_2 is incorporated into the product acids, we further examined the possible intermediates prior to the cut-off of the initial carboxyl group in the decarboxylation of propionic acid by TiO_2 photocatalysis.

Considering that the possible intermediates are not as stable as substrate acids, we employed the in situ analysis technique diffuse reflectance FTIR measurements (DRIFTS) to observe the decarboxylation of propionic acid. In a typical process, propionic acid (100 μmol per g of catalyst, corresponding to less than one monolayer of propionic acid adsorbed on TiO_2 surface) was adsorbed on TiO_2 (Degussa P25 powder) and exposed to UV irradiation in the presence of H_2O and O_2 in an in situ reactor (see details in Experimental Section). The spectrum of propionic acid adsorbed on TiO_2 before irradiation is shown at the top of Figure 1. The positive and negative absorption bands in the spectrum indicate the formation and disappearance of species adsorbed on TiO_2, respectively. The negative hydroxyl bands at 3680 and 3732 cm^{-1} indicate that surface hydroxyl groups of TiO_2 were consumed upon propionic acid adsorption.[17] Meanwhile, as propionic acid was adsorbed on TiO_2 surface, the positive bands at 2890, 2948, and 2982 cm^{-1}, which characterize C−H stretching of the acid, were observed.[18] In the carboxylate region, five bands at 1300, 1430, 1472, 1532, and 1690 cm^{-1} were also identified. Based on previous studies of the identification of absorption bands in the DRIFTS spectrum of acetic acid adsorbed on TiO_2 and considering the structure similarity between acetic acid and propionic acid,[19] these bands can be individually assigned. That is, the bands at 1300 and 1690 cm^{-1} represent molecularly adsorbed propionic acid, while the bands at 1430, 1472, and 1532 cm^{-1} can be attributed to dissociated propionate. Furthermore, a broad band centered at around 3250 cm^{-1} also appeared and can be assigned to surface adsorbed H_2O.[20] A band at about 1625 cm^{-1}, which belongs to H_2O, should also be visible but was overlapped by the strong carbonyl absorption at 1690 cm^{-1}.[20] Other spectra in Figure 1 were collected at different time intervals upon UV irradiation. The intensity of C−H and carboxylate bands all decreased as the reaction proceeded, indicating that propionic acid was continuously decarboxylated and degraded. At the same time, the intensity of the band at 3250 cm^{-1} increased, which can be due to the generation of H_2O as a reaction product.

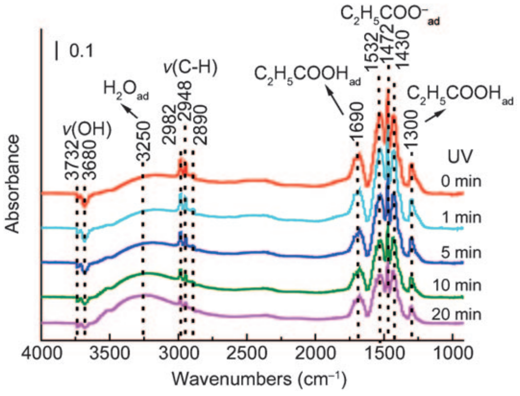


Figure 1. Diffuse reflectance FTIR (DRIFTS) spectra recorded during decarboxylation of propionic acid by TiO_2 photocatalysis. These spectra were collected at different time intervals (from top to bottom: 0, 1, 5, 10, 20 min) upon UV irradiation. The starting concentration of propionic acid was 100 μmol per g of catalyst.

To obtain the information about the generated intermediates in the decarboxylation process, we further subtracted the DRIFTS spectrum collected before UV irradiation from the one after irradiation to get the difference spectrum. The upper spectrum in Figure 2 is the difference spectrum obtained after 1 min of UV irradiation. The appearances of all the negative bands in the alkyl and carboxylate regions of the difference spectrum were consistent with the decarboxylation and degradation of substrate propionic acid. Moreover, an authentic positive absorption peak at 1772 cm^{-1} was observed and indicated the generation of an intermediate in the decarboxylation process. This positive peak at 1772 cm^{-1} could be assigned to the vibration of C=O stretch of a keto group in the intermediate, which should be the α-keto group of pyruvic acid rather than a β-carbonyl group of malonaldehydic acid. Such an assignment is based on two aspects: 1) from intermediate profile, acetic acid could be readily generated from pyruvic acid (Figure S3 in the Supporting Information), while no reasonable shorter-chain acid could be produced from β-carbonyl precursor [Eq. (8)]; 2) the DRIFTS spectrum of pyruvic acid adsorbed on TiO_2 was taken as the standard for comparison and showed a similar absorption peak (Figure S4 in the Supporting Information).

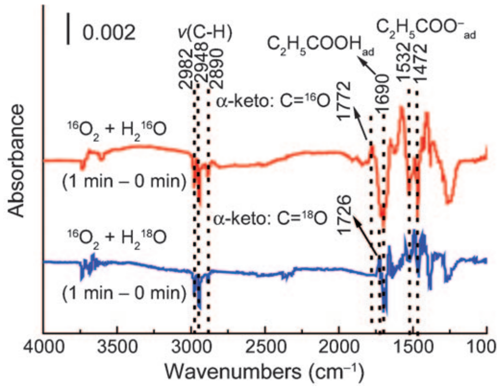
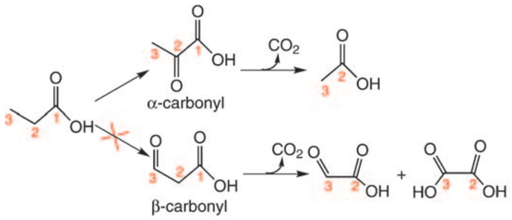
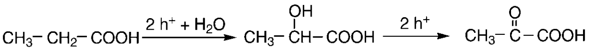


Figure 2. Difference DRIFTS spectra obtained for the decarboxylation of propionic acid by TiO_2 photocatalysis after 1 min of UV irradiation using $H_2{}^{16}O$ (upper line) and $H_2{}^{18}O$ (lower line). The generation of α-keto acid intermediate in the decarboxylation process is indicated by the appearance of positive absorption peaks at 1772 cm^{-1} (upper line) and 1726 cm^{-1} (lower line) in the difference spectra.

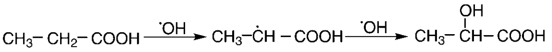


(8)

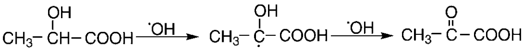
Subsequently, we tried to identify which oxidant, OH radical (generated from H_2O) or O_2, delivers the new oxygen atom in this α-keto group through utilizing $H_2{}^{18}O$ to carry out the same experiment. We found that the peak clearly shifted from 1772 to 1726 cm^{-1} when we replaced ordinary H_2O with $H_2{}^{18}O$ (the lower spectrum of Figure 2). The shift of 46(±4) cm^{-1} induced by isotopic effect fits fairly well with that of 43 cm^{-1} predicted by Hooke's law for this kind of C=O stretch mode, indicating that such an α-keto group was delivered from H_2O through oxidative attack of holes and/or OH radicals rather than dioxygen. In addition, the oxygen exchange between α-keto group of pyruvic acid and $H_2{}^{18}O$ is insignificant at the short timescale of 1 min (Table S2 in the Supporting Information). Thus we conclude that the pristine acids are indeed transformed into α-keto acids prior to decarboxylation. This carbonylation mainly originates from H_2O participation by means of either an electron transfer coupled with hydrolysis process [Eq. (9)] or an α-H abstraction followed by an OH radical-rebound process [Eqs. (10) and (11)]. Alternatively, a process of "one-hole oxidation" followed by the release of another electron from the substrate to the conduction band of TiO_2 could also possibly accomplish this carbonylation [Eq. (12)], similar to the "current doubling" effect observed in the photocatalytic oxidation of alcohols by TiO_2.[13] Such an α-keto acid intermediate should be easily destroyed and thus always exhibited rather weak signal in the difference DRIFTS spectra.



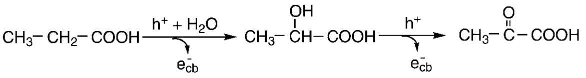
$$CH_3-CH_2-COOH \xrightarrow{2\,h^+ + H_2O} CH_3-\overset{OH}{\overset{|}{C}}H-COOH \xrightarrow{2\,h^+} CH_3-\overset{O}{\overset{\|}{C}}-COOH \qquad (9)$$



$$CH_3-CH_2-COOH \xrightarrow{^{\bullet}OH} CH_3-\dot{C}H-COOH \xrightarrow{^{\bullet}OH} CH_3-\overset{OH}{\overset{|}{C}}H-COOH \qquad (10)$$



$$CH_3-\overset{OH}{\overset{|}{C}}H-COOH \xrightarrow{^{\bullet}OH} CH_3-\overset{OH}{\overset{|}{\dot{C}}}-COOH \xrightarrow{^{\bullet}OH} CH_3-\overset{O}{\overset{\|}{C}}-COOH \qquad (11)$$



$$CH_3-CH_2-COOH \xrightarrow[e^-_{cb}]{h^+ + H_2O} CH_3-\overset{OH}{\overset{|}{C}}H-COOH \xrightarrow[e^-_{cb}]{h^+} CH_3-\overset{O}{\overset{\|}{C}}-COOH \qquad (12)$$

Now that an intermediate in the decarboxylation process has been successfully identified, and this intermediate was determined to mainly originate from H_2O participation, O_2 would reasonably take part in the subsequent transformation; that is, the decarboxylation of this pyruvic acid intermediate to an acetic acid product. Theoretically, the participation of O_2 should be accompanied by photogenerated electrons (or other active free radicals) to accomplish the transformation, since inactivated triplet O_2 cannot directly react with pyruvic acid. Therefore, we refer to the well-defined electrochemical experiment in which electrons either accumulated in the conduction band of TiO_2 film electrode or were readily taken away through tuning external current.[15] As this is a dark experiment, the net reaction of pyruvic acid with conduction band electrons (e^-_{cb}) and O_2 can be directly examined and the influence of holes/OH radicals is avoided. In a typical process, a cathodic bias potential (1.6 V vs. NHE) was continuously applied to a TiO_2 film electrode in an electrochemical cell that was filled with aerated pyruvic acid solution. In this way, we can simulate the photogeneration of electrons in the conduction band of TiO_2 without UV illumination so that holes and/or OH radicals are no longer generated. Consequently, we could directly observe whether this pyruvic acid precursor reacts with e^-_{cb} and dioxygen to implement decarboxylation (Figure 3).

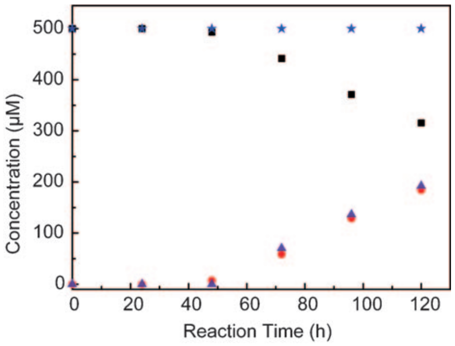
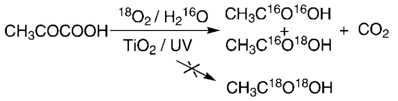


Figure 3. Temporal concentration changes of various acids in the electrochemical reactions using pyruvic acid (■) and propionic acid (★) as substrates. The concentrations of decomposed pyruvic acid (●) and produced acetic acid (▲) in the pyruvic acid reaction are also shown here. In the reactions, a cathodic bias potential (1.6 V vs. NHE) was continuously applied to the TiO_2 film electrode without UV irradiation.

Within this dark electrochemical reaction, pyruvic acid was indeed decomposed and converted to acetic acid slowly but quantitatively (with almost 100% selectivity). That is, only acetic acid, rather than any less than C_2 acid (i.e., formic acid) or keto-, aldehyde-, dicarboxylic acids, was generated in this process. For comparison, we also took propionic acid as the initial substrate in the electrochemical reaction to observe its behavior under the same conditions and found no evident decarboxylation processes. These results adequately illustrate that the intermediate α-keto acid is crucial for e^-_{cb} and O_2 to give rise to the decarboxylation of a carboxylic acid. In contrast to the situation of general TiO_2 photocatalytic reactions, H_2O_2 was not detected during all the electrochemical reactions, which indicates that O_2 may play a different role in the transformation of α-keto acid to shorter-chain acid from that of capturing e^-_{cb} to be converted into H_2O_2 or other active oxygen derivates.[2,3] Accordingly, O_2 definitely participates and reliably achieves the decarboxylation of propionic acid through being activated by e_{cb}^- without the aid of holes and/or OH radicals as soon as propionic acid is transformed into α-keto acid. Note that the α-keto acid could also be transformed to shorter-chain acid by the oxidation of holes and/or OH radicals;[21] the transformation of the α-keto acid intermediate to product acid can be realized by both hole/OH radical pathway and electron/O_2 pathway.

Based on the above discovered characteristics of the decarboxylation process, we can draw the outline of one tandem reaction in which O_2 is involved in the integrated decarboxylation process: the substrate acid is transformed to α-keto acid by holes or OH radicals, then the α-keto acid further releases CO_2 to afford a shorter-chain monoacid by the synergistic effect of e_{cb}^- and O_2. For the last step, the clarification of the contribution of this reaction pathway to practical TiO_2 photocatalytic reactions is needed as this transformation could also be realized by the oxidation of holes and/or OH radicals. Thus, we designed an $^{18}O_2$ (95 %) isotopic-labeling experiment to examine the transformation of pyruvic acid to acetic acid by TiO_2 photocatalysis (Table 3), which enables us to directly observe the distribution of oxygen atoms from O_2 or H_2O in newly established carboxyl groups. The incorporation of an oxygen atom from $^{18}O_2$ was clearly indicated by the generation of $CH_3C^{16}O^{18}OH$. Moreover, no single $^{18}O^{18}O$ profile in produced acetic acid illustrates that at least one oxygen atom of the substrate α-keto acid remains in the new carboxyl group as the old C^1–C^2 bond is cleaved, supporting our protocol for the specific α-scission of CO_2.

Table 3. The transformation of $CH_3COCOOH$ by TiO_2 photocatalysis using $^{18}O_2$ and the isotopic distribution of produced CH_3COOH.[a]



	Conversion[b] [%]	Yield[c] [%]	Percentage of various CH_3COOH isotopomers[d] [%]		
			$^{16}O^{16}O$	$^{16}O^{18}O$	$^{18}O^{18}O$
1	44.3	29.5	99.8	0.2	0
2	69.0	44.9	91.5	8.5	0
3	84.9	52.9	84.4	15.6	0
4	96.1	56.3	77.3	22.7	0
5	100.0	55.9	75.9	24.1	0

[a] Experimental conditions: solution of pyruvic acid in $H_2^{16}O$ (10 mL, 10 mM) in a 50 mL vessel. [b] The conversion of pyruvic acid. [c] The fractional yield of acetic acid, which was calculated according to yield = *c* (generated acetic acid)/*c* (converted pyruvic acid). [d] Calculated by the integration of corresponding peak area obtained from mass spectrometry.

Similar to the trend of dioxygen incorporation in the corresponding $H_2^{18}O$ isotopic-labeling experiment (Table S3 in the Supporting Information), a gradual increase in the proportion of $CH_3C^{16}O^{18}OH$ (from 0.2 to 24.1 %) was observed along with the increase of conversion yield, corresponding to a gradually enhanced participation of O_2. To our knowledge, such an unexpected phenomenon that the proportion of O_2 entrance into products depends on the conversion of substrates in TiO_2 photocatalytic reactions has not been reported before. A possible explanation for the origination of this phenomenon is that α-keto acids may take the priority of adsorption compared to non-substituted acids at TiO_2 surface defects,[22] at which four-coordinate Ti (Ti_{4c}) sites are available for the simultaneous coordination of substrates and O_2.[23] While at five-coordinate Ti (Ti_{5c}) sites on the terrace of TiO_2 surface, the α-keto acids and non-substituted acids should be chemisorbed in identical fashion and affords no significant differences in absorption priority.[24] Henderson et al. have similarly illustrated that substrate and O_2 adsorption play determining roles in the control of selectivity between isobutene and isobutane as the product of gas-phase photodecomposition of trimethyl acetate (TMA) on $TiO_2(110)$.[25] At a fixed initial TMA coverage and in the presence of O_2, the photodecomposition selectivity switches from initially isobutene to the mixture of isobutene and isobutane and then back to predominantly isobutene within this reaction, in which the latter selectivity change originates from the enhanced impact of O_2 at decreased substrate concentration.[25] However, further studies are evidently needed to get the accurate conclusion about this process.

Conclusion

Through isotopic-labeling examinations combined with DRIFTS and electrochemical experiments, we have illustrated an unexplored O_2-involved pathway for the decarboxylation of saturated carboxylic acids by TiO_2 photocatalysis. An alternative pathway, involving e_{cb}^- and O_2, exists in addition to the direct hole/OH radical oxidation pathway and affords the decarboxylation of carboxylic acids by TiO_2 photocatalysis. Through this way, the C^1–C^2 bond cleavage of the initial saturated straight-chain carboxylic acid is accomplished in two steps: at first, the pristine acid is oxidized to α-keto acid by holes or OH radicals without loss of carbon atoms; and then, the intermediate α-keto acid is decarboxylated to shorter-chain acid through the e_{cb}^-/O_2 process, in which an oxygen atom of O_2 is selectively incorporated into product acid.

Experimental Section

Materials and general instrumentation: Formic acid, acetic acid, propionic acid, butanoic acid, and valeric acid were obtained from Acros. Pyruvic acid was purchased from Sigma–Aldrich. All the acids were of analytical grade purity and used as received. $H_2^{18}O$ was purchased from Jiangsu Changshu Chemical Limited. The isotopic enrichment was 96 % as determined by mass spectrometry. $^{18}O_2$ was purchased from Cambridge Isotope Laboratories, Inc. The isotopic enrichment was 95 %. Conducting glass sheets (< 20 Ω per square, Laibao Technologies Limited, transparent conductive oxide coated glass plates of fluorine-doped SnO_2) were employed as substrates for TiO_2 film coating. Deionized and doubly distilled water was used throughout this study.

Kinetic runs were analyzed by ion chromatography (IC). Samples of approximately 0.5 mL were taken out at regular time intervals during the irradiation. The concentrations of carboxylic acids and their degradation intermediates were measured by a DX-120 ion chromatograph with an IonPac AS11 column (Dionex). The eluent was 0.8 mM $NaHCO_3$ solution. The flow rate was $0.5\,mL\,min^{-1}$. The identification of the intermediates by IC was preformed by comparing the retention times with those of standards. Total organic carbon (TOC) was measured by a Tekmar Dohrmann Apollo 9000 TOC analyzer. The detection of H_2O_2 was performed using standard DPD-POD method.[26]

GC-MS analyses were carried out on a Finnigan Trace GC ultra gas chromatograph with a 25 m DB-5 column, coupled with a Finnigan Trace DSQ mass spectrometer. The injector port was set for split operation at 250 °C. The temperature program of the column was as follows: at 80 °C, hold time = 5 min. The isotopic enrichment of various acids was examined by EI-MS. Response factors for the isotopomers of these acids were within a small experimental error and thus it was assumed that all isotopomers would also have identical response factors.

Photocatalytic tests for kinetic and isotopic studies: The photocatalytic degradation reactions of carboxylic acids for kinetic studies were all performed with a TiO_2 film (anatase), which was prepared and characterized according to the method described in our earlier study.[15] The photoactive area of the TiO_2 film was $6\,cm^2$. The reactions were carried out in Pyrex vessels (50 mL) with a solution volume of 30 mL. The initial concentration of all the substrate acids was 2 mM. Irradiations were carried out using a 100 W mercury lamp (Toshiba SHL-100UVQ-2).

In all the isotopic labeling experiments, a TiO_2 film with a photoactive area of $3\,cm^2$ was used. The photocatalytic reactions of propionic acid and pyruvic acid in $H_2{}^{18}O$ were carried out in Pyrex vessels (10 mL). A solvent volume of 1.5 mL was used each time. The initial concentration was 20 mM for propionic acid and 10 mM for pyruvic acid, respectively. Irradiations were carried out using a 500 W Xe lamp (Beijing Trusttech Co. Ltd.). The photocatalytic reactions of pyruvic acid using ${}^{18}O_2$ were performed in Pyrex vessels (50 mL). A solution volume of 10 mL at initial acid concentration of 10 mM was used each time. Before the ${}^{18}O_2$ reaction, the solution in the vessel was placed under vacuum with a pump and then purged with argon three times to remove the air, followed by saturation with ${}^{18}O_2$. Irradiations were carried out with a 100 W mercury lamp (Toshiba SHL-100UVQ-2). After the isotopic-labeling reaction was stopped, the solution was extracted by ethyl ether. Then the ethyl ether was evaporated and the resulting liquid was analyzed by GC-MS.

DRIFTS measurements: A Thermo Nicolet 6700 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector was used for the diffuse reflectance FTIR measurements (DRIFTS). A praying mantis diffuse reflectance accessory and a reaction cell equipped with a heater (Harrick Scientific) form the reaction system. Degussa P25 powder was housed at a sample cup inside the reaction cell. A dome covered the cell containing three windows. Two of the windows were made of ZnSe and permitted entry and exit of the infrared beam and the diffusely scattered infrared light while the third one was used for UV irradiation (quartz). A constant flow of 100 sccm of 20 % O_2 and 80 % N_2 was maintained throughout the reaction. UV irradiations were performed with a 500 W Xe lamp (Beijing Trusttech Co. Ltd.).

The TiO_2 powder was heated to 360 °C and kept at this temperature for 20 min to provide a clean catalyst surface. Then the catalyst was cooled to 30 °C and the spectrum of the TiO_2 surface was collected. Interferograms over the range of 650 to $4000\,cm^{-1}$ were recorded by averaging 100 scans with a resolution of $4\,cm^{-1}$. A processing time of 0.6 min was needed for one spectrum. Before every experiment the background spectrum was collected and then subtracted from subsequent spectra after the introduction of reaction substrates. Afterwards a pulse of the substrate acid (100 μmol per g catalyst) was injected into the reaction cell (as the real density of five-coordinate Ti surface sites on the ideal $TiO_2(110)$ surface is about $10^{-5}\,mol\,m^{-2}$,[27] less than one monolayer of acid molecules could be obtained in the experiment considering the specific BET surface area of about $50\,m^2g^{-1}$ for P25). Spectra were continuously collected with gas flushing excess acids away from the TiO_2 surface until they get stable. For the reaction with $H_2{}^{16}O$ or $H_2{}^{18}O$, a pulse of $H_2{}^{16}O$ or $H_2{}^{18}O$ was respectively injected into the reaction cell.

Electrochemical measurements: The electrochemical reactions of the acids with the conduction band electrons and O_2 were performed in a two-compartment reactor and standard two-electrode mode. The electrodes consisted of a TiO_2 film working electrode and a Pt foil counter electrode. The two electrodes were separated in different compartments of the reactor. The electrolyte used was 0.01 M $NaClO_4$. The active area of the TiO_2 electrode was $6\,cm^2$. A potentiostat model DJS-292 was used to bias the TiO_2 electrode and to measure the electrochemical parameters. A cathodic bias potential (1.6 V vs. NHE) was applied to the TiO_2 electrode. The initial concentration of all the substrate acids was 0.5 mM.

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