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Photocatalytic Decarboxylation of Lactic acid by Pt/TiO₂

Received 00th January 20xx, Accepted 00th January 20xx Kaituo Liu,^a Anton Litke,^a Yaqiong Su,^a Bart G. van Campenhout,^a Evgeny A. Pidko ^{a,b,*} and Emiel J.M. Hensen ^{a,*}

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A photocatalytic route for the conversion of lactic acid to acetaldehyde in water is demonstrated. Direct UV photolysis of lactic acid yields CO_2 and ethanol via a radical mechanism. Pt/Ti O_2 considerably increases the rate of lactic acid decarboxylation with acetaldehyde, H_2 and CO_2 as the main products. A concerted photodecarboxylation/dehydrogenation mechanism is proposed.

In the last decade, substantial progress has been made towards viable chemocatalytic processes for upgrading the carbohydrate fraction of biomass into valuable chemical products (Figure 1a).¹ Dehydration and hydrogenation are common chemical reactions employed in catalytic sugar conversion.² Although, from an energy-efficiency point of view, selective decarboxylation chemistry is advantageous compared to the dehydration, it is out of reach of current chemocatalysis.³

Nature employs enzyme-catalysed decarboxylation in glucose metabolism (Figure 1b).⁴ Conversion of glucose (C6) involves retro-aldolization and dehydrogenation into two pyruvate (C3) molecules, followed by decarboxylation and hydrogenation steps to produce ethanol (EtOH).⁵ The retroaldolization step to C3 intermediates can also be carried out by chemocatalysts.⁶ Highly efficient systems for the production of lactic acid (LA) and its esters from cellulosic biomass based on heterogeneous Sn-BEA zeolite^{7, 8} or homogeneous Pb(II) catalysts⁹ have been reported. Selective conversion of LA into C2 chemicals is much more difficult: decarboxylation of α hydroxy carboxylic acids remains a challenge to organic chemistry.³ Earlier studies have evidenced the utility of photochemistry to enable such transformation. It has been shown that EtOH and CO₂ can be obtained by decomposition of LA with UV light.¹⁰⁻¹⁴ The conversion of α -hydroxy carboxylic



Figure 1. (a) Cellulose and hemicellulose represent the major fraction of lignocellulosic biomass that can be converted to useful chemicals such as EtOH or LA via (b) biochemical reaction paths or via (c) chemocatalytic reaction paths developed here.

acids with a supported Pt photocatalyst has been described by Harada *et al.* in the early 1980s.^{11,12} More recent photocatalytic studies consider LA merely as a biomass-derived sacrificial electron donor for H₂ production.^{14, 15} Herein we explore the potential of photochemistry for constructing new pathways for biomass valorization. We present photochemical and photocatalytic LA conversion to C2 chemicals and highlight its broader scope by demonstrating one-pot photocatalytic coupling reactions with alcohols (Figure 1c).

Irradiation of aqueous solutions of LA by full-wavelength light (Hg(Xe) lamp, 500 W) yields EtOH and CO₂ as the main products as determined by a combination of GC-MS, 2D HSQC NMR (Figure S6a), GC-TCD and HPLC analysis (Table 1, entries 1-4). No LA conversion was observed without UV irradiation or by irradiation at λ > 360 nm. Direct photolysis also produced small amounts of 2,3-butanediol (BD) and HCOOH (FA). The increasing yield of these by-products at higher LA concentration (Table 1, entries 1-4) points to a radical mechanism (Figure 2). The reactions yield equal amounts of C1 (CO₂ and FA) and C2 products (EtOH and BD). AcH (acetaldehyde), AcOH (acetic acid) and propionic acid are formed in minor amounts (Table 1).

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UV-Vis spectroscopy in combination with time-dependent density functional theory (TD-DFT) calculations demonstrate that deep UV (λ < 250 nm) excitation is required for C-C bond activation in LA (Figure S2, Figure S5). UV spectra of aqueous LA contain a distinct absorption band at 225 nm (E = 5.51 eV) attributed to intramolecular charge transfer (Figure S2). TD-DFT calculations at the B3LYP/6-311+G(d,p) level with implicit polarized continuum model (PCM) corrections to account for water predict a $S_0 \rightarrow S_1$ excitation in free LA at an energy of 6.02 eV (λ = 206 nm, Table S2). DFT calculations further show that the activation barrier for decarboxylation of LA in the ground S₀ state is higher than 200 kJ/mol. The preferred pathway will be via decarboxylation of LA in the first excited (S_1) state (Figure S5) with a computed barrier of 61 kJ/mol. These results explain why UV photoexcitation is required to cleave the C-C bond resulting in LA decarboxylation via a radical mechanism.

Aiming at improving the reaction efficiency, we studied the use of titania-supported noble metal photocatalysts (NM/TiO₂, NM = Au, Pt, Pd and Ru). Commercial TiO₂ pigment (Aeroxide P25) was chosen as the support because of its good performance and high stability under photocatalytic conditions¹⁶. The results of the photocatalytic tests are summarized in Table 1 (entries 5-9). TiO₂ alone inhibits photochemical conversion (Table 1, entry 5), resulting in trace amounts of reaction products.

Table 1. Photochemical conversion of aqueous solutions of LA with and without TiO₂-supported noble metal photocatalysts (NM/TiO₂). $^{[a]}$

| # | C ₀ (LA)/Cat ^[b] | | Yields, μmol ^[c] Yield ^Σ , % ^[d] | | | | | | | |
|---|--|------|---|------|-----|-----|--------|-------|----|----|
| | | AcH | EtOH | AcOH | BD | FA | CO_2 | H_2 | C1 | C2 |
| 1 | 0.02 M/- | 0 | 76 | 1 | 21 | 9 | 146 | 0 | 16 | 12 |
| 2 | 0.05 M/- | 1 | 135 | 0 | 34 | 32 | 209 | 0 | 10 | 8 |
| 3 | 0.10 M/- | 2 | 279 | 26 | 144 | 75 | 466 | 0 | 11 | 11 |
| 4 | 0.50 M/- | 6 | 850 | 24 | 227 | 412 | 839 | 0 | 5 | 5 |
| 5 | TiO ₂ | 7 | 44 | 0 | 19 | 0 | 104 | 0 | 2 | 2 |
| 6 | Pt/TiO ₂ | 2014 | 22 | 78 | 5 | 0 | 2030 | 2083 | 41 | 41 |
| 7 | Au/TiO₂ | 974 | 39 | 16 | 14 | 0 | 989 | 1000 | 20 | 21 |
| 8 | Pd/TiO₂ | 1300 | 6 | 55 | 0 | 62 | 1300 | 1245 | 27 | 26 |
| 9 | Ru/TiO₂ | 1684 | 19 | 110 | 3 | 63 | 1669 | 1724 | 35 | 34 |

[a] Conditions: H₂O solvent 50 mL, 20 °C, 3 h, full output of 500 W Hg(Xe) arc lamp, for catalytic experiments 50 mg 1 wt% NM/TiO₂(P25) catalyst used; [b] Initial LA concentration/catalyst, # 5 to 9: C₀(LA)=0.1 M; [c] Ethyl lactate and propionic acid detected with less than 1% yield; [d] Decarboxylation yield of C1 (CO₂ and HCOOH) and C2 (EtOH+AcH+BD+AcOH) product equivalents.



Figure 3. (a) Evolution of CO₂ during photochemical conversion of aqueous LA (0.1 M) under full-wavelength (FW) and $\lambda > 360$ nm irradiation in the absence (photolysis) and presence of TiO₂-supported 1 wt. % noble metal catalysts. (b) Comparison of the time-yield profiles for the main gas- and liquid-phase products of the photocatalytic LA conversion with Pt/TiO2 under FW irradiation of Hg(Xe) lamp.

The loading of a small amount (1 wt%) of noble metals on TiO₂ drastically changes the reaction outcome (Figure 3a, Table 1, entries 6-9). Compared with direct photolysis of LA, the NM/TiO₂ photocatalysts afford two- to four-fold higher decarboxylation yields. Photocatalysts also shift the selectivity from predominantly EtOH and CO₂ to AcH, CO₂ and H₂. Only small amounts of EtOH, AcOH, BD and FA are observed (Figure 3b), indicating that the photocatalytic reaction follows a different mechanism from that of direct LA photolysis. Strikingly, the selectivities to AcH, CO₂ and H₂ are nearly independent of the noble metal. On the other hand, the noble metal strongly affects the reaction rate (Figure 3a) and, hence, the overall (Table 1). Pt/TiO₂ displays the highest photocatalytic performance with a decarboxylation yield of 41 % after 3 h reaction that is nearly four-fold higher than the yield in the direct photolysis. Photocatalytic activity decreases in the order Pt/TiO₂>Ru/TiO₂>Pd/TiO₂>Au/TiO₂.

In separate photoelectrochemical measurements Pt/TiO_2 shows the highest response in an aqueous LA electrolyte (Figure S7). This suggests that, similar to photocatalytic reduction of water, electrons photogenerated in titania are removed by proton reduction during photocatalytic conversion of LA.^{17, 18} ¹⁹ NM nanoparticles facilitate H₂ evolution by trapping photogenerated electrons, which improves charge carrier separation and lowers H₂ evolution overpotential.^{19, 20}

We carried out additional experiments using the best Pt/TiO₂ catalyst in an aqueous EtOH to check whether the primary pathway in LA conversion proceeds via EtOH as an intermediate. Photoreforming of EtOH results in three-fold lower H₂ evolution rate compared with the LA photodecarboxylation (Table S3). Combined with the observation that nearly equivalent amounts of AcH, ${\rm H}_2$ and CO₂ irrespective of the activity level are obtained during photocatalytic LA conversion, we propose that photocatalytic reaction proceeds in a single step involving decarboxylation and dehydrogenation without the intermediate formation of EtOH. We also established that LA does not undergo photocatalytic conversion over Pt catalysts supported on Al₂O₃ or CeO₂ under identical conditions (Table S5).

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Figure 4. (a) Proposed mechanism for photocatalytic LA conversion at the Pt/TiO₂ interface. (b) FTIR spectroscopy and periodic DFT (pDFT) calculations evidence a facile reaction of surface OH groups of TiO₂ with LA to form surface lactates upon exposure of Pt/TiO₂ to LA vapor at RT (1 + LA \Rightarrow 2 + H₂O). (c) TD-DFT predicts that such TiO₂-bound lactate can undergo a ligand-to-metal charge transfer excitation that facilitates a one-step decarboxylation (2 \Rightarrow 3). Next, the photo-assisted H₂O dissociation (3 + H₂O \Rightarrow 4 + CO₂ + CH₂CHO) regenerates surface OH groups and produces Pt-bound H species, which recombine resulting in H₂ evolution that closes the catalytic cycle (4 \Rightarrow 1 + H₂).

The photocatalytic nature of the reaction is underpinned by studying the influence of the excitation wavelength (Figure 3a). Compared with full wavelength irradiation, the activity of Pt/TiO₂ at $\lambda > 360$ nm – the value close to the absorption edge of P25 TiO₂ – decreases substantially. However, without the catalyst, irradiation with $\lambda > 360$ nm does not lead to any conversion of LA. These data show the importance of photo-induced electron-hole separation in TiO₂ during photocatalytic decarboxylation of LA, and also highlight the possibility of carrying out photocatalytic dehydrogenative decarboxylation of LA under solar irradiation.

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On the basis of the above findings, we can propose a reaction mechanism for the photocatalytic conversion of LA by Pt/TiO₂ (Figure 4a). The mechanism is also supported by (TD-)DFT calculations and vibrational spectroscopy (Figure 4b and c). The catalytic cycle starts with the reaction of LA with a surface OH group of TiO₂, resulting in a surface-bound lactate intermediate and water $(1 + LA \rightarrow 2 + H_2O)$, Figure 4a). The surface of hydrated titania will contain hydroxyl groups.²¹ In agreement with previous publicatons,²² infrared spectra of TiO₂ and Pt/TiO₂ before and after exposure to LA confirm its reaction with hydroxyl groups of the support (Figure 4b).

calculations²³ Periodic dispersion-corrected DFT+U (PBE+D3/PW-400 eV, U_{eff} = 4.0 eV for 3d orbital of Ti²⁴) were carried out on a Pt₁₀/rutile-TiO₂(110) model (Figure 4b) to gain better insight into the proposed mechanism (Figure S9). Rutile titania was chosen, as we found that Pt is slightly more active on rutile TiO_2 than on anatase TiO_2 (Figure S9). The (110) surface is one of the most stable rutile titania surfaces.²⁵ The 10-atom Pt cluster allows studying the interface between Pt and the TiO₂ support. Periodic DFT simulations indicate that the substitution of a titania-bound surface hydroxyl group with LA at the Pt/TiO₂ interface is barrier-less and highly exothermic (Figure 4b). Next, proton abstraction from the α -OH group of the adsorbed lactate by the Pt cluster occurs simultaneously with C1-C2 bond cleavage to yield CO_2 and AcH ($2 \rightarrow 3$, Figure 4a). This reaction step, which results in the reduction of one Ti(IV) center to Ti(III), is kinetically and thermodynamically unfavourable in the ground state. At the Pt/TiO_2 surface it requires overcoming a barrier higher than 200 kJ/mol (IM4 \rightarrow TS2 \rightarrow IM5, Figure S10). As computational modelling of periodic surface structures in the excited state is too demanding, we carried out excited state calculations on a simplified model system in the framework of the TD-DFT method using a trinuclear cluster $Ti_3O_6(H_2O)_6H^+$ model, which represents the surface lactate species (Figure 4c). These calculations predict a pronounced shift of the charge-transfer band to lower energies by 1.5 eV for the lactate-titania adsorption complex as compared with free LA and the lactate anion (Figure 4c and Table S6). This shift is in a qualitative agreement with the experimental observations. The catalytic cycle is closed by re-oxidation of the Ti(III) site by water $(3 \rightarrow 4,$ Figure 4a). This reaction is facilitated by the photo-generated electron-hole pair, regenerating the initial Ti-OH group and another H atom bound to Pt that leads to H₂ formation via $\mathbf{4} \rightarrow$ $1 + H_2$.



Figure 5. Acceptorless dehydrogenative coupling (ADC) of lactic acid in (a) ethanol leading to acetaldehyde diethyl acetal (ADEA) and (b) in methanol leading to acetaldehyde dimethyl acetal (ADMA).

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Biological pathways from glucose to ethanol start with glycolysis, which converts glucose into pyruvate followed by decarboxylation into AcH, which is then hydrogenated to EtOH (Figure 1b). Herein we described a chemocatalytic path for decarboxylative acceptorless dehydrogenation (DAD) of LA to AcH that does not involve pyruvate as an intermediate. Only traces of pyruvic acid by-product were observed in the photocatalytic runs and the conversion of pyruvic acid itself was not influenced by the presence of Pt/TiO₂ (Table S4).

Acceptorless dehydrogenation (AD) and acceptorless dehydrogenative coupling (ADC) chemistry²⁶ provide atomefficient approaches for the oxidation of organic molecules.²⁷ We explored the possibility of carrying out similar chemistry starting from LA and alcohols using our photocatalytic approach that activates LA (Figure 5). The H₂ yield in these experiments is higher than in water due to photocatalytic solvent dehydrogenation (Figure S12a).²⁸ Carrying out the reaction in EtOH results in acetaldehyde diethyl acetal (ADEA), which is the coupling product of decarboxylative acceptorless dehydrogenation of LA with EtOH (Figure 5a). No such coupling product was observed upon photoreforming of ethanol by Pt/TiO₂ (Table S3). The ADEA yield was 26 % after 3 h reaction (Figure S12c). We found that the overall coupling process is photocatalytic as mixing acetaldehyde and ethanol in the dark at room temperature did not lead to ADEA with or without catalyst (Figure S13). The reaction in MeOH produces a much higher H₂ yield due to the high reactivity of MeOH towards photoreforming. The liquid phase products are paraformaldehyde and the acetaldehyde dimethyl acetal (ADMA) (Figure 5b).

In summary, LA can be efficiently decarboxylated into EtOH and AcH under photochemical and photocatalytic conditions, respectively. Direct photolysis requires deep UV light excitation with λ < 250 nm and produces EtOH and CO₂ via a radical mechanism. Photodecarboxylation of LA can be catalysed by titania-supported noble metal nanoparticle catalysts. We propose a concerted surface-mediated decarboxylative dehydrogenation mechanism, which yields stoichiometric amounts of AcH, CO₂ and H₂. Noble metal nanoparticles promote dehydrogenation of lactate. Photocatalytic decarboxylation of LA provides а chemocatalytic option in the proposed artificial pathway from carbohydrate biomass to C2 products.³ We have also demonstrated the potential of this chemistry to novel atomefficient acceptorless dehydrogenative coupling paths converting biobased chemicals into value-added products.

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