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Green oxidation of bio-lactic acid with H_2O_2 into tartronic acid under UV irradiation[†]

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Tartronic acid (TA) is a high value-added chemical widely used as a pharmaceutical product and a preservative; however, its synthesis technology is complicated and high cost. In this study, aqueous solutions of lactic acid were photochemically converted into TA *via* green oxidation by using hydrogen peroxide (H_2O_2).

Tartronic acid (TA) or hydroxymalonic acid is a high valueadded fine chemical¹⁻³ used to treat various disorders, such as osteoporosis and obesity. Dompe Farmaceutici, an Italian pharmaceutical company, was the first to report that TA derivatives exhibit positive effects on bone metabolism; this property allows the use of TA derivatives as bone-sparing agents to treat osteopenic disorders.4 TA is an anticorrosive and protective agent used to prevent oxidative decomposition of food.5,6 The applications of TA are currently limited to high value-added field because of the high cost1,7 of this reagent (US \$ 1564 g^{-1}). The TA market is dominated by Johnson Matthey Company and Alfa Aesar, which use maleic acid as a starting material via permanganate oxidation to prepare this reagent. The selective partial oxidation of glycerol with heterogeneous catalysts is a more cost-efficient way to prepare and obtain TA. However, many products can be obtained during glycerol oxidation; thus, the challenge is to find suitable catalysts that are selective to the desired product. Kimura et al. employed cerium and bismuth as promoters for palladium- or platinumbased catalysts with active carbon as a support for glycerol oxidation and achieved 58% yield of sodium tartronate at full conversion. Cai et al.7 reported that glycerol oxidation over Aubased catalyst yielded 80% TA at 60 °C under 0.3 MPa O2. Thus, the development of inexpensive and environmentfriendly methods to prepare TA presents a challenge.

Biomass⁸⁻¹¹ is a promising candidate that can serve as a sustainable source of organic carbon to produce fuels, chemicals, and carbon-based materials. Lactic acid^{12,13} (2-hydroxypropanoic acid) containing adjacent hydroxyl and carboxylic groups can be considered to be a model of an overfunctionalized biomass-derived molecule. It can be obtained from biomass at a low cost by bacterial fermentation and has a growing market because of its multiple applications. Previous studies have reported the direct conversion of lactic acid to products such as acrylic acid,14,15 propanoic acid,16 pyruvic acid,17 and 2,3-pentanedione¹⁸ by dehydration, reduction, oxidation and condensation. Traditional catalytic methods often exhibit poor atomic economy and are carried out under rather harsh (e.g., strongly basic) conditions, so it is better to develop new methods that could be operated under mild conditions with rapid reaction and little environmental pollution.

In the traditional lactic acid oxidation reaction, the α -C could be selective catalytic activated¹⁷ in the presence of catalysts, which means lactic acid were dehydrogenated and converted to pyruvic acid. In this study, we propose a new strategy in which lactic acid was oxidized by hydroxyl radicals ('OH) and selectively converted to TA. Under UV irradiation, hydrogen peroxide (H₂O₂) aqueous solution led to the production of hydroxyl radicals ('OH), which have the capability of oxidizing a variety of organic molecule. But, in our research we were able to selectively oxidize the methyl of lactic acid molecules to carboxyl group by controlling the reaction time and the amount of H₂O₂. As a result, selective oxidation of the methyl group of the lactic acid molecule was the main reaction path.

Table 1 summarizes the experimental results of the conversion of a 0.5 M lactic acid aqueous solution under different conditions. When a small volume of hydrogen peroxide solution was added into the solution, the lactic acid was oxidized under UV light irradiation (entry 1 in Table 1). The data indicate that the main liquid products of lactic acid oxidation were TA, mesoxalic acid (MA), acetic acid (HAc), and gas products mainly consisting of CO_2 , as well as small amounts of CO and CH_4 . Control experiments were carried out to investigate the influence of H_2O_2

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Entry

1

2

 3^b

 $\mathbf{\Delta}^{c}$

CH₄

Trace

Trace

0

0

CO

0.87

4.08

0

0

Table 1 The conversion and selectivity for lactic acid oxidation in different experimental conditions^a

5.13

0



^a Reaction condition: 0.5 M lactic acid aqueous solution, 200 mL; H₂O₂ with different quantity; atmosphere, argon; temperature, 20 °C; light source, 300 W high-pressure Hg-lamp; irradiation time, 30 min. ^b 0.5 M lactic acid aqueous solution without added H_2O_2 . ^c Dark reaction of the same reactant.^d The addition amount of reactants are listed in the table.

0

o

Trace

0

0

0

and light, a single reaction of the lactic acid solution mainly produced HAc and CO₂ under UV light, and the conversion rate was very low (entry 3 in Table 1). When appropriate of hydrogen peroxide solution was added into the lactic acid solution, no chemical reaction occurred in the dark (entry 4 in Table 1). Control experiments indicated hydroxyl radicals produced from the photolysis of H₂O₂ is required to initiate this reactions.

Reactant^d [mol]

 $0.04H_2O_2 + 0.1HL$

0.1HL

As a safe and clean oxidizing agent, hydrogen peroxide exhibits active chemical properties. This compound presents an environmentally benign profile because it decomposes into water and oxygen as its only reaction products. The UV/H₂O₂ system is an advanced oxidation process in which H₂O₂ is decomposed under UV light to generate hydroxyl radicals ('OH) as highly reactive oxygen species. Generally, the UV/H2O2 process¹⁹⁻²¹ can lead to complete mineralization of organic carbon to CO₂ and H₂O. Thus, the control of hydroxyl radical reaction and attainment of a highly value-added chemical present a challenge. In our study, we found methyl of lactic acid was selectively oxidized to carboxyl, thus make lactic acid conversion into TA. UV light catalyzes the dissociation of H_2O_2 into hydroxyl radicals through chain reactions; these oxidants then react with lactic acid molecules in aqueous solutions. However, optimization of the peroxide dose is highly critical because excess peroxide can further oxidize lactic acid into CO₂ (entries 2 in Table 1). To evaluate the effect of H_2O_2 supply on TA selectivity from the oxidation of lactic acid, a series of experiments were performed using 0.5 mol L^{-1} lactic acid.

The effects of H2O2 supply on lactic acid conversion and TA selectivity are shown in Fig. 1a. TA selectivity reached a maximum of 0.04 mol H₂O₂ supply and then gradually decreased when the H₂O₂ supply further increased. Meanwhile, the selectivity of acetic acid slowly increased. The effects of H₂O₂ supply on CO₂ formation during the experiments were evaluated using GC techniques. As shown in Fig. S1,† increasing the H₂O₂ supply resulted in a steady increase in CO₂ formation. With an increase in H₂O₂ dosage, plenty of hydroxyl radicals generated within a short time prompt the over-oxidation of lactic acid, which can produce CO₂ in large quantities. Thus, effectively control the amount of H2O2 was key point of improving TA selectivity. The influence of reaction duration on TA selectivity was investigated. As illustrated in Fig. 1b, TA selectivity increased with increasing reaction duration and reached 39.9% after 20 min. However, when the reaction duration was prolonged, the TA selectivity gradually decreased while the acetic acid selectivity slowly increased. The TA selectivity reached a maximum and then gradually prolongation of the reaction time could be due to the content of H₂O₂ decreased because the photolysis speed of H₂O₂ is very fast during the experiments. Thus, we examined the changes in H2O2 and 'OH concentrations over time. Fig. 2a shows the changes in H_2O_2 concentrations over time; the curve shows the rapid occurrence of H₂O₂ photolysis during the first few minutes and the complete decomposition of H2O2 after 30 min. Fig. 2b shows the fluorescence intensity at 425 nm originating from 'OH, which increased with reaction time; the intensity reached its maximum at 15 min and then decreased rapidly. H₂O₂ was

30.10

0



Fig. 1 (a) Effect of the H_2O_2 supply on the selectivity of liquid products from the oxidation of lactic acid, (b) effect of reaction time on the production from the oxidation of lactic acid



Fig. 2 (a) Effect of illumination time on the photolysis of H_2O_2 , (b) PL spectral changes observed during irradiation of H_2O_2 in the solution of terephthalic acid (excitation at 315 nm).

depleted in the solution; such depletion might have caused the decline in TA selectivity over time. Fig. S2[†] shows that the production rate of CO₂ varied with time; this rate rapidly increased during the first 10 min and then decreased slowly over time. At the start of the first reaction time, lactic acid was further oxidized into CO₂ because of the excessive 'OH in the reaction system; the rate of CO₂ production began to decrease as H_2O_2 was gradually consumed.

The intermittent supplementation of lactic acid and H_2O_2 is beneficial to keep these compounds at optimal proportions, thereby effectively increasing the TA selectivity because of the high photolytic rate of H₂O₂ during the experiments. Fig. 3a shows the influence of the intermittent supplementation of lactic acid and H₂O₂ within a 30 min interval during the oxidation of lactic acid. During these operations, lactic acid conversion (Fig. S3[†]) tended to exhibit the same increasing tendency in each cycle, and the TA selectivity (Fig. 3a) remained constant while the concentration of TA (Fig. 3b) showed upward trend throughout the experiment. The MA selectivity also remained fairly constant; meanwhile, the HAc selectivity gradually increased during the process (Fig. S4[†]). TA gradually accumulated through the supplementation of lactic acid and H₂O₂ at the 30 min interval; hence, the process has great significance in practical applications for mass production.

As shown in the aforementioned experiments, lactic acid conversion slowly declined, whereas the TA selectivity exhibited no increasing trend over time with intermittent supplementation of lactic acid and H_2O_2 (Fig. 3), possibly because TA was photolyzed under UV light irradiation. Thus, we examined TA photolysis at varying concentrations. Fig. 4a shows that the photolysis rate of TA was lower under UV irradiation. So, the effect of photolysis on TA selectivity can be ignored, possibly because TA photolysis occurred faster when H_2O_2 was added in the presence of UV. Moreover, UV/H_2O_2 has been found to increase the oxidation rate of various organic compounds.



Fig. 3 The effect of the TA selectivity (a) and concentration (b) by intermittent supplementation of 2 mL lactic acid and 4 mL H_2O_2 .

Therefore, we compared the photolysis of lactic acid and TA in the UV/H_2O_2 process. As shown in Fig. 4b, the photolytic rate of lactic acid was higher than that of TA; however, photolysis was markedly accelerated with the addition of H_2O_2 . This result may explain why the TA selectivity was maintained to a certain extent.

The generation of TA under UV light irradiation in the presence of H_2O_2 is explained by proposing the following reactions. UV irradiation of H_2O_2 in aqueous solution leads to the production of hydroxyl radicals ('OH) (eqn (1)), thus initiating the cleavage of C–H bonds²² by dehydrogenating the organic substance; this process can simultaneously accept



Fig. 4 (a) The photolysis of TA in the different concentrations, (b) the photolysis of lactic acid and TA in the UV/H_2O_2 process (*n* means the photolysis amount of TA or lactic acid, n_0 means the initial amount of TA or lactic acid, n/n_0 means the degradation ratio).

another 'OH to form intergradation. In our experiment, 'OH reacting with CH_3 -CH(OH)-COOH formed $(OH)CH_2$ -CO-COOH intermediates (eqn (2)). In this process, the methyl group of lactic acid dehydrogenated and combined with hydroxyl radicals to form $(OH)CH_2$ -CO-COOH. These intermediates further reacted with 'OH to form $(OH)_2CH$ -CH(OH)-COOH (eqn (3)), which was highly unstable and rapidly converted into HOC-CH(OH)-COOH (eqn (4)). Furthermore, HOOC-CH(OH)-COOH (eqn (5)). The potential side reactions involved are expressed in eqn (7)-(11). In these pathways, CH_3 -CH(OH)-COOH was further oxidized into HOOC- $C(OH)_2$ -COOH, CH_3COOH , and CO_2 .

$$H_2O_2 \to 2^{\circ}OH \tag{1}$$

$$\label{eq:CH3-CHOH} \begin{array}{l} \mbox{CH}_3\mbox{-}\mbox{CH}(\mbox{OH})\mbox{-}\mbox{COOH}\mbox{+}\mbox{2}\mbox{OH}\\ \mbox{-}\mbox{OH}\mbox{OH}\mbox{-}\mbox{CH}(\mbox{OH})\mbox{-}\mbox{COOH}\mbox{+}\mbox{H}_2\mbox{O} \end{array} (2)$$

$$\begin{array}{l} (OH)_2 CH-CH(OH)-COOH \\ \rightarrow HCO-CH(OH)-COOH + H_2 O \end{array} \tag{4}$$

$$\begin{array}{l} \text{HCO-CH(OH)-COOH + 2'OH} \\ \rightarrow \text{HOOC-CH(OH)-COOH + H}_2\text{O} \end{array} \tag{5}$$

$$\begin{array}{rl} \mbox{CH}_3\mbox{-}\mbox{CH}(\mbox{OH})\mbox{-}\mbox{COOH} + 3\mbox{H}_2\mbox{O}_2 \\ \mbox{\rightarrow HOOC-CH}(\mbox{OH})\mbox{-}\mbox{COOH} + 4\mbox{H}_2\mbox{O} & (6) \end{array}$$

 $\begin{array}{l} \text{HOOC-CH(OH)-COOH + 2'OH} \\ \rightarrow \text{HOOC-C(OH)_2-COOH + H_2O} \end{array} \tag{7}$

CH₃--CH(OH)--COOH + 'OH

 $\rightarrow \text{`CH(OH)CH}_3 + \text{CO}_2 + \text{H}_2\text{O}$ (8)

 $CH(OH)CH_3 + OH \rightarrow CH_3CHO + H_2O$ (9)

 $CH_3CHO + 2 OH \rightarrow CH_3COOH + H_2O$ (10)

 $2CH_3COOH + 6 OH \rightarrow 4CO_2 + 2H_2O + 5H_2$ (11)

The equation for the overall reaction is presented in (eqn (6)). From this equation, we can speculate that the optimal reaction of the mole ratio of H_2O_2 to lactic acid is 3. However, during the actual experiments, the addition amount of H_2O_2 in large quantities can easily cause further oxidation of lactic acid. Thus, the amount of H_2O_2 should be controlled within a proper range.

Conclusions

Lactic acid can be converted into TA, a high-value fine chemical under UV irradiation conditions with H_2O_2 as an oxidant. The experiments demonstrated that the TA selectivity reached 39.9% under optimal conditions and remained almost unchanged after intermittent supplementation of lactic acid and H_2O_2 to keep these compounds within optimal proportions. Overall, the results present important implications for the development of a green route for biomass transformation with high efficiency.

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