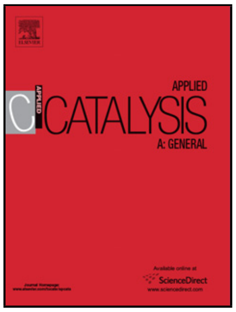

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Levulinic acid upgrade to succinic acid with hydrogen peroxide

Davide Carnevali[a,b], Marco G. Rigamonti[a], Tommaso Tabanelli[b], Gregory S. Patience[a], Fabrizio Cavani[b, *]

[a]Polytechnique Montreal, Chemical Engineering department, 2900 Edouard Montpetit Blvd, Montreal, H31 1J4, QC, Canada

[b]Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Universitá di Bologna, Viale del Risorgimento, 4, 40136, Bologna, Italy

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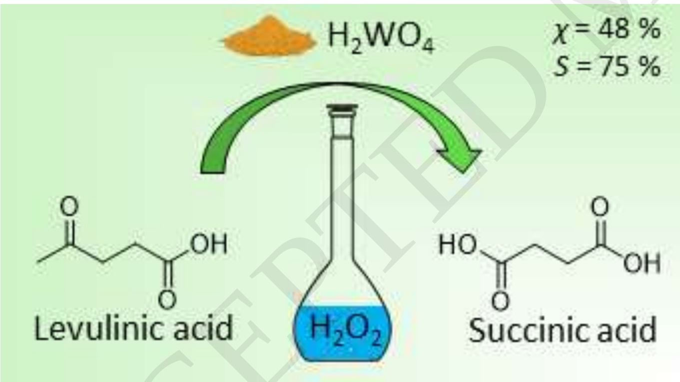

Highlights

- Solvent-free conversion of levulinic acid to succinic acid with hydrogen peroxide and H_2WO_4
- Formation of an adduct between the catalyst and the substrate, which enhances the

regioselectivity

- Maximum conversion of 48 % with 75% selectivity to succinic acid, after 6 h
- A new green process for synthesize succinic acid from bio-sourced levulinic acid

Abstract

Levulinic acid is produced from the acidic aqueous degradation of 5-hydroxymethylfurfural, with potential applications in bio-value added chemicals synthesis. Here, we report for the first time, the Baeyer-Villiger oxidation of levulinic acid to succinic acid, with hydrogen peroxide and tungstic acid at mild conditions and without any organic solvent. We investigated the effects of time, amount of reagent-to-catalyst molar ratio and H_2O_2-to-levulinic acid molar ratio. The maximum succinic acid selectivity was 75 % with a levulinic acid conversion s high as 48 %, after 6 h at 90°C. We propose a reaction mechanism based on results obtained from the reactivity of the intermediates. The catalyst interacts with the substrate, forming a cyclic species that enhances the formation of succinic acid versus 3-hydroxypropanoic acid.

Keywords: levulinic acid, succinic acid, hydrogen peroxide, Baeyer-Villiger, oxidation, tungstic acid, H_2WO_4

1. Introduction

Biomass is a primary source of energy and a potential feedstock for bio-chemicals. Compared to fossil fuels, it has an elevated oxygen-to-carbon ratio, which makes it more suitable for the synthesis of highly functionalized value-added molecules, like to 5-hydroxymethylfurfural (HMF) by fructose dehydration [1,2]; a further oxidation of the intermediate forms 2,5-

furandicarboxylic acid (FDCA) [3,4]. The dehydration of fructose occurs with high temperature or by the presence of an acidic Brønsted catalyst. The main synthesis hurdle is that HMF degrades in aqueous acidic condition, and forms insoluble polymers (humins), or cleaves to make levulinic acid (LEV) and formic acid. Most works in this area apply multi-phasic reactors [4], membrane reactors [5] or ionic liquids [6] to reduce humins.

LEV is an important bio-building block for valeric acid [7], methyltetrahydrofuran [8], alkyl levulinate [9], diphenolic acid [10], δ-amino levulinic acid, γ-valerolactone [11,12], α-methylene-γ-valerolactone [13] and succinic acid. Derivatives applications regard mainly the production of rubber, plasticizers, pharmaceuticals and textiles [14]. Biomass is the preferred starting material to produce LEV [15–17]. LEV and succinic acid are in the top 10 value added chemicals from biomass [18,19]. The succinic acid market value reached 400 billion USD per year [20]. Industrially, the favored route to succinic anhydride is the hydrogenation of maleic anhydride, derived from fossil *n*-butane [21]. On the contrary, the main bio-pathway is the sugars fermentation.

LEV reacts with basic, acidic and metal oxide catalysts to form succinic acid; most studies add solvent to increase product yield (Table 1). One promising reaction is the Baeyer-Villiger oxidation with hydrogen peroxide as an oxidizing agent. Adding catalyst increases the reaction rate and improves the selectivity to the desired products. Examples of catalysts include alumina [22], tungstic acid [23], tin [24], titanium silicalite-1 (TS-1) [25], selenium [26] and bio-enzymes [27]. The mechanism comprises the nucleophilic addition of a hydroperoxide anion to the carbonyl carbon [28]. Environmental conditions modulate the intermediate rearrangement; acidic catalysts react with the substrate to form the methyl ester, while in basic conditions it produces the acetate through an intramolecular addition. Starting from humic acids, hydrogen peroxide achieved 93 % malonic acid or 62 % succinic acid [29].

Table 1: Review of the conversion with reaction parameters and yields. LEV: levulinic acid; M-LEV: methyl levulinate; SUCC: succinic acid; M-SUCC: methyl succinate; DM-SUCC: dimethyl succinate; MA: maleic anhydride.

Reagent	T, °C	Catalyst	Solvent	Time, h	Products	Yield, %	Ref.
LEV	300 – 400	V_2O_5			SUCC		[30]
LEV	40 – 60	V_2O_5 + HNO_3		1 - 4	SUCC		[31]
LEV	150	Ru-based magnetic nano particles + O_2	H_2O	6	SUCC	78	[32]
LEV	90	Mn-based catalyst	AcOAc	10	SUCC, MA	9, 26	[33]
M-LEV	80	Amberlyst-15 + H_2O_2	Methanol	6	M-SUCC	41	[34]
LEV	200	K_2CO_3	Dimethyl carbonate	6	DM-SUCC	21	[35]
Furfural	80	Amberlyst-15 + H_2O_2	H_2O	24	SUCC	74	[36]
LEV	25	I_2	*t*-BuOH	1	SUCC	87	[37]

Wu et al. [38] described the basic oxidation of LEV with H_2O_2 to 3-hydroxypropionic acid (HPA), a precursor of acrylic acid. On the contrary, hydrogen peroxide, combined with sulfuric acid, achieved a maximum of 48 % succinic acid selectivity. Replacing H_2SO_4 with trifluoroacetic acid, increased selectivity to 62 %, at 90 °C after 2h [39].

Here for the first time, we describe the acidic, organic solvent-free Baeyer-Villiger oxidation of LEV to succinic acid with H_2O_2 and H_2WO_4. We investigated the effects of time, reagent:catalyst ratio and H_2O_2:LEV ratio on LEV conversion and on the main products selectivity. Furthermore, we investigated the reaction pathway, testing the intermediates reactivity.

2. Experimental

2.1. *Materials*

We used all reagents without further purification. The purity of LEV was greater than ≥ 97 %, succinic acid > 99 %, formic acid purity varied between 95 % to 97 %, propionic acid > 99.5 %, α-angelica lactone purity was 98 %, malonic acid was 99 %, and stabilized hydrogen peroxide 27 % w/w in H_2O), sulfuric acid (ACS reagent, 95 % to 98 %) and potassium permanganate (97 %) from Sigma Aldrich. Glacial acetic acid (ACS Reag. Ph Eur) was acquired from Carlo Erba, while oxalic acid (98 % anhydrous) from Acros Organics. We purchased the 3-hydroxypropionic acid sodium salt from Toronto Research Chemicals. The tungstic acid (99 %) catalyst was purchased from Sigma Aldrich.

2.2. Catalytic experiment

We designed a full factorial set of experiments with 3 factors and 3 levels each (27 tests) with the statistical software Minitab®. The reactions time were at 1 h, 3 h, 6 h, with a LEV:H_2WO_4 ratio of 100:1, 50:1, 10:1 and H_2O_2:LEV ratio of 1.5:1, 3:1, 5:1. An oil bath kept the temperature constant at 90 °C. We derived the sample standard deviation, *s* (Table 2), by repeating experiments at three different conditions.

Table 2. Repetition of three tests at various conditions. * H_2O_2:LEV molar ratio, ** LEV: H_2WO_4 molar ratio. Conversion (X) and Selectivities (S) are in %. Succ: succinic acid; acet: acetic acid; mal: malonic acid; oxal: oxalic acid, form: formic acid, AL: α-angelica lactone; HPA: 3-hydroxypropionic acid; gly+glyox: glycolic acid and glyoxylic acid; prop: propionic acid.

	Conv	S_{succ}	S_{acet}	S_{mal}	S_{oxal}	S_{form}	S_{AL}	S_{HPA}	$S_{gly+glyox}$	S_{prop}
Sample standard deviation *s*	2	2	0.5	0.3	0.3	0.2	1	0.4	0	0.3

We investigated the reaction pathway, evaluating the reactivity of the intermediates at 1 h and 6 h, with a LEV:H_2WO_4 molar ratio of 100 and H_2O_2:LEV molar ratio of 5.

In a standard reaction procedure, we added 5 mmol (0.58 g) of LEV into an Erlenmeyer flask, with the specified amount of catalyst (H_2WO_4, i.e. 0.124 g for a LEV:H_2WO_4 molar ratio of 10) and H_2O_2 solution (aqueous solution 27 % w/w, i.e. 0.93 g for a H_2O_2:LEV molar ratio of 1.5). The mixture was homogenized for few minutes, while an oil bath heated it to the desired temperature (90°C). The flask was equipped with a reflux condenser to avoid an excessive evaporation of the solution. By means of gas-chromatography we qualitatively analyzed the non-condensable gases inside the flask, which turned out to contain CO_2. At the end of the test, the mixture was cooled rapidly from 90 °C down to room temperature, diluted with distilled water and filtered using a disposable syringe equipped with 0.20 μm PTFE filter to preserve the HPLC column.

Tungstic acid is insoluble in cold water (only slightly soluble in hot water), however in the presence of H_2O_2 the catalyst is soluble in the state of pertungstic acid (H_2WO_5). This means that working at high H_2O_2 conversion would favor the precipitation of the catalyst facilitating its recovery by filtration [40].

For catalyst recycle tests, we put the mixture in the rotavapor, in order to completely evaporate water and traces of residual H_2O_2. In order to remove the adsorbed organic compounds, the catalyst was washed with acetone, and dried in the oven at 80 °C overnight. This procedure allowed to recover the 70% of the initial H_2WO_4 amount, in the form of a yellow solid.

2.3 *Analytical procedure*

A Varian CP-3380 gas chromatography equipped with a packed Carbosieve SII column (2m length, stationary phase of active carbons of 80-100 mesh) was used to analyze the non-condensable gases. A TCD monitored the concentration of CO, CO_2, O_2 and N_2, with He as the carrier gas. The oven was maintained at 40°C for 7 min, then the temperature was ramped up until 220°C with a rate of 30°C/min, and finally left isothermal for 10 min.

An HPLC Agilent Technologies 1260 Infinity, equipped with an Aminex HPX-87H Ion Exclusion column (300 mm x 7.8 mm), maintained at 30 °C, measured the concentration of the crude products. The autosampler injected 10 µL of the solution, while the eluent was a 5 mM H_2SO_4 solution, flowing at 0.4 mL min^{-1}. The instrument monitored the response of the samples at 8 wavelengths (from 210 nm to 284 nm). The LEV conversion (Eq. 1) and the products selectivity based on carbon (Eq. 2) were calculated as follows:

$$X_{LEV} = \frac{n_{LEV}^{i} - n_{LEV}^{fi}}{n_{LEV}^{i}} \cdot 100 \tag{1}$$

$$S_{PROD} = \frac{n_{PROD}^{f}}{n_{LEV}^{i} - n_{LEV}^{f}} \cdot \frac{\vartheta_{PROD}}{\vartheta_{LEV}} \cdot 100 \tag{2}$$

where n^{i}_{LEV} and n^{f}_{LEV} are the initial moles and the final LEV moles in the system, n^{f}_{PROD} the final moles of product analyzed by HPLC. ϑ_{LEV} and $\vartheta_{\mathrm{PROD}}$ are the number of carbon atoms of LEV and products.

We evaluated the amount of unconverted hydrogen peroxide with a 0.3 N potassium permanganate solution and a diluted 1:4 aqueous sulfuric acid solution. The titration proceeded with the addition of distilled water and 10 mL of acidic solution to the sample. We titrated the sample using a calibrated burette until the solution turned permanent pink [41]. The mass percentage of H_2O_2 by (Eq. 3):

$$H_2O_2, \%\ \mathrm{g\ g^{-1}} = \frac{mL_{KMnO_4} \cdot N_{KMnO_4} \cdot 0.0170 \cdot 1000}{g_{sample}} \tag{3}$$

where N is the normality of the $KMnO_4$ solution, $\mathrm{mL_{KMnO_4}}$ is the volume of permanganate used for the titration and 0.0170 is the mass per milliequivalent of H_2O_2.

3. Results and discussion

3.1. LEV reactivity and selective oxidation

Reactivity screening tests at three H_2O_2 concentration (H_2O_2:LEV molar ratio of 1:1, 1.5:1 and 3:1), three temperatures (50 °C, 70 °C and 90 °C) and constant H_2WO_4:LEV molar ratio of 100 demonstrated a very low LEV conversion, reaching a minimum of 5 % at the lowest temperature and peroxide content (Test 31, Table 3). Increasing the temperature led to an increased conversion of LEV. Therefore, all the further experiments were carried out at 90 °C.

Time, catalyst mass and H_2O_2 content affect succinic acid selectivity and LEV conversion (Figure 1, Table 3). The maximum variation of conversion was recorded at H_2O_2:LEV ratio of 3 and LEV:H_2WO_4 ratio of 50; the value increased from 28 % after 1 h to 46 % after 6 h reaction time (Table 3, entries 13 and 15). Addition of H_2O_2 and H_2WO_4 amplified the oxidative power and the acidity of the reaction media, enhancing the reactivity of the substrate. The highest LEV conversion was shown at 6 h, reaching 57 % at the highest hydrogen peroxide concentration and catalyst loading (Table 3, entry 27). Furthermore, at these conditions, we recorded the highest conversion after 1 h of reaction (Figure 1).

Succinic acid selectivity increased from 10 % (Table 3, entry 1) to 49 % (entry 9) with increasing H_2O_2 and time. Increasing the H_2WO_4, its behavior changed; at 50:1 LEV:H_2WO_4 molar ratio, the selectivity increased with peroxide concentration, reaching a maximum after 3 h, but then decreased (entries 10-18). This trend was accentuated at higher catalyst loading, where the highest selectivity was registered after 1 h, and then decreased with time (entries 19-27). Figure 2 summarizes the effect of the two main reaction parameters on selectivity to succinic acid at 3 h.

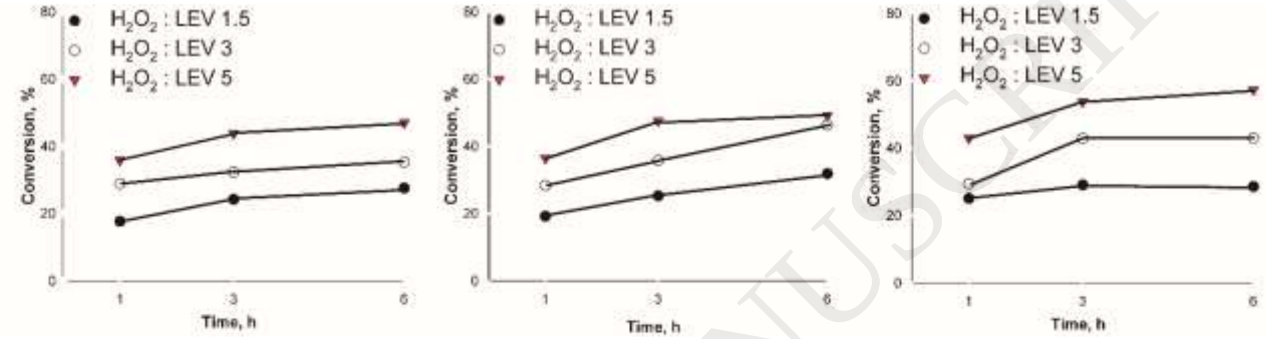

Figure 1 Effects of various amount of H_2O_2 and H_2WO_4 on the conversion at 1 h, 3 h and 6 h. LEV:H_2WO_4 molar ratio: 100 (left figure), 50 (middle), 10 (right).

We measured acetic acid, malonic acid, oxalic acid, formic acid, α-angelica lactone, 3-hydroxypropionic acid, propionic acid, glycolic acid and glyoxylic acid concentration by means of HPLC (Table 3). Some intermediates reacted further to CO_2 and volatile compounds [42], which were undetected. Acetic acid was the main by-product and it formed in all tests. Many compounds decomposed to this acid, which accounts for its high selectivity, and increased with H_2WO_4 and H_2O_2 concentration and longer time. Selectivity to acetic acid approached 10 % after 1 h, and rose to 20 % after 6 h. The highest selectivity was 23 % (Table 3, entry 23). We detected low concentrations of oxalic acid in all the reactions, but it never exceeded 5 %, and mainly remained below 1 %. Oxalic acid easily oxidizes in the presence of acidic oxidizing environment, releasing CO_2 [43]. For LEV:H_2WO_4 catalytic ratio higher than 50, selectivity hardly were higher than 1 %, while at ratio of 10, values increased from 2 % to 5 %.

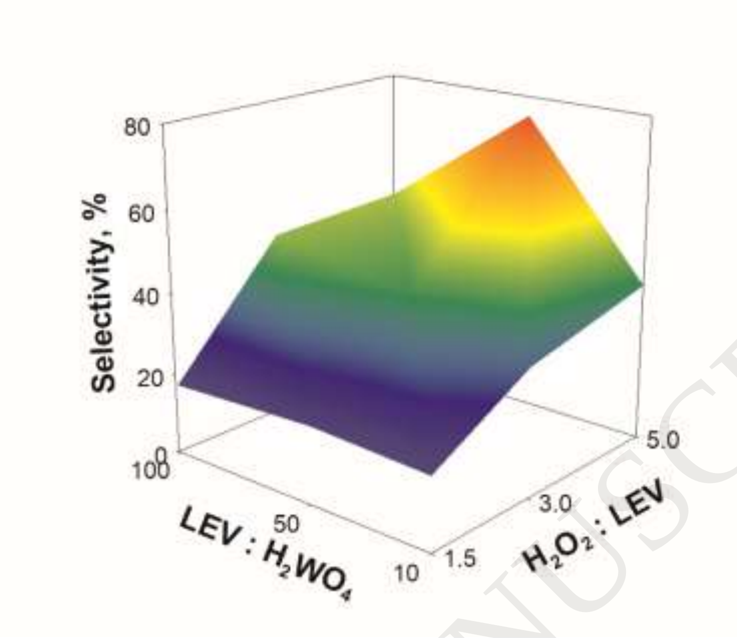

Figure 2 Succinic acid selectivity reached a maximum with the highest concentration of H_2O_2 and LEV:H_2WO_4 ratio of 50, after 3 h.

Glycolic and glyoxylic acids showed low selectivity, which remained almost always lower than 1 %. Formic acid presented a similar trend: selectivity varied between 0 % and 5 %, with a general increase with time and H_2WO_4 loading. Results at low H_2O_2 concentration showed that the absence of reactive oxygen stopped the Baeyer-Villiger oxidation, favouring the dehydration of LEV to α-angelica lactone. In acidic conditions and low H_2O_2 concentrations (LEV:H_2O_2 molar ratio 1:1), selectivity to α-angelica lactone was 50 % from LEV. At higher H_2O_2 concentration, α-angelica lactone degraded to acetic acid and malonic acid (Table 4). α-Angelica lactone selectivity decreased with reaction time and was the greatest with low tungstic acid loading (Table 3, entries 1, 4 and 7): at 1 h, 3 h, and 6 h, selectivity dropped from 38 % down to 21 %, and 14 %, respectively. In experiments at a 1.5:1 H_2O_2:LEV ratio and 100:1 LEV:H_2WO_4

ratio, after 1 h the lactone selectivity was 38 %, but dropped to 2 % after 6 h (entries 1-3). This behavior could be attributed to the degradation of the lactone, which is highly unstable in the presence of oxidizing agents and acids. Selectivity to the lactone was very high in experiments carried out with a H_2O_2:LEV ratio of 0.5 (entries 28-30).

The selectivity to 3-hydroxypropionic acid was always lower than 4 % with the lowest H_2O_2 concentration. However, the selectivity increased with H_2O_2 concentration and reached 25 % at a H_2O_2:LEV ratio of 5:1 (entries 8 and 9 in Table 3). Generally, the selectivity reached a maximum after 3 h, and then slowly decreased. Furthermore, higher H_2WO_4 loading boosted the reactivity of 3-hydroxypropionic acid, resulting in selectivity values lower than 1 %.

Succinic acid may decarboxylate to propionic acid. At the highest amount of H_2WO_4 (low LEV:H_2WO_4 ratio) almost no propionic acid was detected, due to its degradation to acetic acid and CO_2. The highest values of propionic acid selectivity were shown with the lowest catalyst loading and highest hydrogen peroxide concentration, reaching a selectivity of 6 % (Table 3, entries 8 and 9).

Table 3 Effects of time, H_2WO_4 and H_2O_2 content on conversion and selectivity. * H_2O_2:LEV molar ratio, ** LEV:H_2WO_4 molar ratio. Succ: succinic acid; acet: acetic acid; mal: malonic acid; oxal: oxalic acid, form: formic acid, AL: α-angelica lactone; HPA: 3-hydroxypropionic acid; gly+glyox: glycolic acid and glyoxylic acid; prop: propionic acid.

*** Test 31 at 50 °C, adding one drop of H_2O_2 every 10 seconds, and at the end leaving the reaction run for 20 min more

Exp	H_2O_2*	H_2WO_4**	Time, h	Conv, %	S_{succ}, %	S_{acet}, %	S_{mal}, %	S_{oxal}, %	S_{form}, %	S_{AL}, %	S_{HPA}, %	$S_{gly+glyox}$, %	S_{prop}, %
1	1.5	100	1	18	10	14	5	0.7	2	38	1	4	0.6
2	1.5	100	3	24	17	18	7	0.7	3	4	3	0.1	2
3	1.5	100	6	28	19	20	7	2	3	2	4	0.2	0.3
4	3	100	1	29	10	8	6	0.3	0.6	21	4	2	2
5	3	100	3	32	47	13	6	0.6	0.9	0.2	14	0.5	3
6	3	100	6	35	48	17	6	0.8	1	0.3	11	0.1	3
7	5	100	1	36	2	3	3	0.2	0.4	14	0.6	0.5	4
8	5	100	3	44	48	8	4	0.4	1	0.6	25	0.1	6
9	5	100	6	47	49	12	4	0.5	1	2	25	0	6
10	1.5	50	1	19	12	11	5	0.8	3	29	1	0.2	0.5
11	1.5	50	3	25	19	17	8	3	3	3	3	0.2	0.3
12	1.5	50	6	32	18	18	6	2	3	2	2	0.2	0.1
13	3	50	1	28	32	4	3	0.3	0.2	9	0	0.1	2
14	3	50	3	36	41	18	7	2	2	1	11	0.2	3
15	3	50	6	46	29	22	5	2	2	4	3	0.2	0.5
16	5	50	1	37	23	1	2	0.1	1	10	0	0	2
17	5	50	3	48	75	9	4	0.7	0.6	3	15	0.1	5
18	5	50	6	49	71	17	4	0.9	0.8	0	12	0.1	3
19	1.5	10	1	25	35	13	7	5	3	4	1	2	0.2
20	1.5	10	3	29	18	19	8	3	4	3	1	0.2	0
21	1.5	10	6	43	11	13	4	2	3	0	1	0.2	0
22	3	10	1	29	62	9	9	5	3	6	2	0	0.9
23	3	10	3	43	32	23	7	5	4	3	1	0.2	0.6

24	3	10	6	32	22	20	6	3	5	1	1	0.1	0
25	5	10	1	43	58	12	5	4	2	4	1	1	2
26	5	10	3	54	39	21	5	0.3	3	1	1	1	0.3
27	5	10	6	57	35	22	4	4	3	1	1	0	0
28	0.5	100	1	15	7	5	3	0.3	1	53	0.7	0.4	0.2
29	0.5	100	3	16	10	11	4	0.6	2	50	0.8	0.2	0
30	0.5	100	6	17	7	8	3	0.4	2	49	0.7	0.3	0.1
31***	3	100	0.35	5	6	2	1	0	0	24	0	0	0

In the three experiments at H_2O_2:LEV ratio 0.5:1 and LEV:H_2WO_4 ratio 100:1 (Table 3, entries 28-30), H_2O_2 conversion approached 100 % after 1 h reaction time; in fact, LEV conversion showed a moderate growth, passing from 15 % at the first hour to 17 % after 6 h. Besides the usual by-products, we also detected the formation of acrylic acid (not shown in Table 3); its selectivity was 8 % after 1 h, slightly increasing to 13 % after 3 h and then decreasing down to 10 % after 6 h.

In order to check the stability and recyclability of H_2WO_4, the catalyst was recovered after reaction (see Experimental), and recycled a few times. Differences of catalytic performance between each experiment were within the standard deviation; therefore, the behavior of the recycled catalyst can be considered to be the same as that one of the fresh catalyst (Table S1 in the Electronic Supplementary Information).

3.2. Selectivity versus time

Most of the by-products selectivity were invariant with time (Figure 3): 3-HPA selectivity was 1 %, malonic acid 8 %, formic acid 4 %, oxalic acid about 2 %, whereas α-angelica lactone varied from 0 % to 5 %. Succinic acid selectivity decreased from 35 % to 11 % after 6 h. Acetic acid, the main by-product, reached a maximum of 19 % at 3 h after which it dropped to 13 %. LEV conversion was 25 % after 1 h and increased to 43 % at 6 h. We did not detect the formation of propionic acid.

The total carbon selectivity decreased from 75% after 1 h down to 40-45% after 6 h reaction time. This drop is due to the product overoxidation occurring along with the increasing LEV conversion. We did not close the carbon mass balance due to the formation of volatile molecules (mainly CO_2) that left the reactor and the formation of insoluble polymers, which slightly changed the color of the solution during the reaction. For short reaction times the solution was colourless.

We calculated the H_2O_2 remaining in the reaction mixture by titration. When the hydrogen peroxide was the limiting reagent (H_2O_2:LEV ratio 0.5:1), the oxidant conversion was almost complete (98 %). When the oxidant was in slight excess (ratio 1.5:1), after 1 h reaction time H_2O_2 conversion was 86 % (overall selectivity to oxidised products, calculated with respect to converted H_2O_2, was 56%; therefore, 44% of converted H_2O_2 decomposed), which increased up to 92 % after 3 h (selectivity 54%). Working in large oxidant excess (ratio 5:1) and the highest catalyst loading, the H_2O_2 conversion dropped to 64 %.

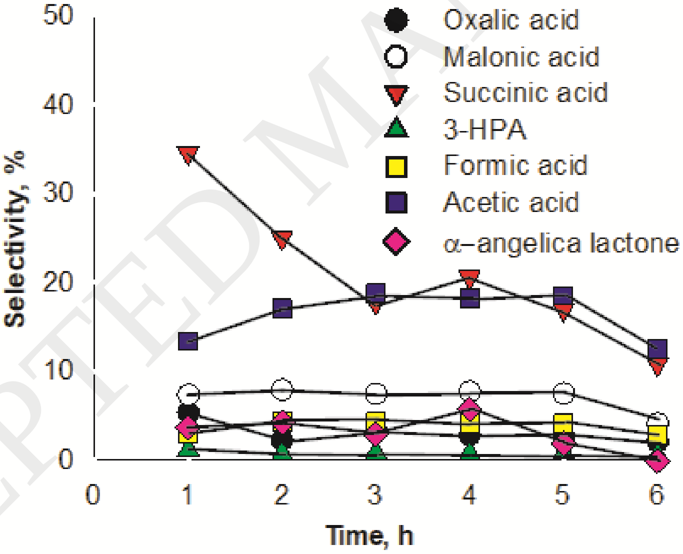

Figure 3 Variation of the selectivity of the products with time. LEV:H_2WO_4 =10 ; H_2O_2:LEV =1.5; T 90 °C.

3.3. The reaction network

The oxidation pathway proceeds with the formation of various by-products and intermediates. The Baeyer-Villiger mechanism consists of the addition of an oxygen atom to convert a ketone to an ester. Oxygen from a peroxide compound attacks the molecule with two competitive mechanisms to form methyl succinate or 3-acetoxypropanoic acid [37]. Moreover, in the presence of an acidic environment or high temperature, LEV dehydrates to α-angelica lactone [44] (Figure 4).

Wu et al. [38] found that the regioselectivity of the Baeyer-Villiger oxidation with hydrogen peroxide is pH controlled: under alkaline conditions the insertion of oxygen is favored on the secondary carbon, leading to the 3-acetoxypropanoic acid intermediate and subsequently to 3-HPA and acetic acid, with 50 % yield. In strong acidic conditions - trifluoroacetic acid as solvent - the migration of the less substituted carbon is favored. This mechanism produces methyl succinate as the intermediate, with subsequent acidic cleavage of the ether to methanol and succinic acid, with 60 % yield. As a side reaction, 10 % 3-HPA is also recovered [39].

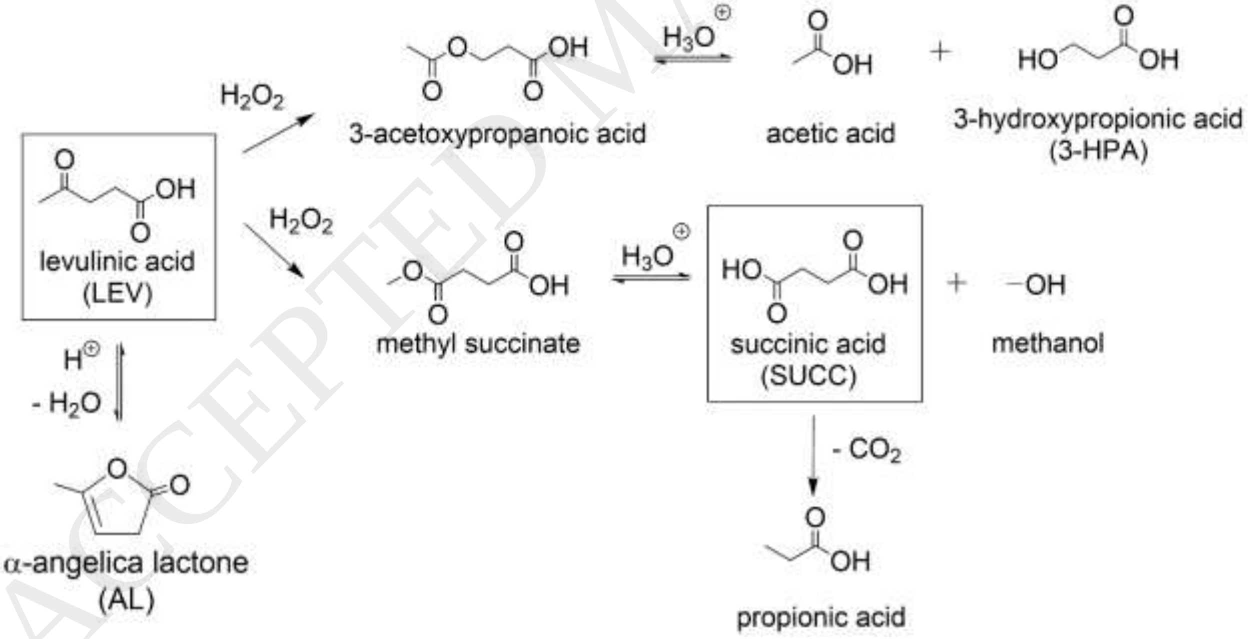

Figure 4. Hydrogen peroxide adds an oxygen to LEV with two competitive mechanisms. The first leads to 3-acetoxypropanoic acid and consequently to 3-HPA, while the second produces methyl succinate, which is in equilibrium with succinic acid.

Methanol can further react with H_2O_2 to form oxidized derivatives: formaldehyde, formic acid and finally CO_2, but MeOH and CH_2O were absent in the HPLC chromatogram traces. These compounds oxidize to CO_2 in the presence of hydrogen peroxide.

3-HPA, formed by hydrolysis of 3-acetoxypropanoic acid, can dehydrate to acrylic acid in the absence of oxidizing agents [45], or can follow the retro-aldolic reaction to acetic acid and formaldehyde. The latter, in an oxidizing environment reacts to formic acid [39]. In an alternative pathway, oxidation of the hydroxy group of 3-HPA gives malonic acid [46].

In order to confirm that the reaction network was similar also with our catalyst and reaction conditions, we carried out experiments by testing the reactivity of both succinic acid and main by-products/intermediates, using the lowest level of H_2WO_4 and the highest of H_2O_2, at 1 h and 6 h reaction time (Table 4).

The experiments with succinic acid as substrate demonstrated an increase in the conversion with time, from 1 % registered after 1 h reaction time to 7 % after 6 h. Those low values provided evidence for the high stability of the product in the reaction mixture. Decarboxylation of succinic acid led to propionic acid, which further can lose a molecule of CO_2 producing acetic acid. Propionic acid selectivity reached 10 % after the first hour of reaction, and consequently dropped to 1 % at 6 h (Table 4).

In tests carried out starting from propionic acid, the acid conversion slightly increased from 18 % to 25 % along with the increase of reaction time. The main products were glycolic and glyoxylic acid and acetic acid. The firsts remained almost constant after 6 h at 5%, while the acetic acid increased from 0.6 % to 3 %. It is worth noting that in the experiments with succinic acid we did not detect the presence of glycolic/glyoxylic acid.

Experiments carried out starting from 3-HPA confirmed the oxidising pathways proposed in the literature; at the end of the reaction, we detected acetic acid, malonic acid, oxalic acid and formic acid. Formic acid selectivity attested at 7 %, while acetic acid was around 22 % and malonic acid around 6 %.

Table 4 Oxidation of the intermediates and the by-products at T 90 °C, reactant:H_2WO_4 molar ratio 100 and H_2O_2:reactant ratio 5. Succ: succinic acid; acet: acetic acid; mal: malonic acid; oxal: oxalic acid, form: formic acid, AL: α-angelica lactone; HPA: 3-hydroxypropionic acid; gly+glyox: glycolic acid and glyoxylic acid; prop: propionic acid

Reagent	t, h	Conv	S_{succ}	S_{acet}	S_{mal}	S_{oxal}	S_{form}	S_{AL}	S_{HPA}	$S_{gly+glyox}$	S_{prop}
Succinic acid	1	1	-	0	0	1	0	0	0	0	10
Succinic acid	6	7	-	3	4	6	1	0	0	0	1
Malonic acid	1	72	-	1	-	17	2	-	0	6	0.4
Malonic acid	6	70	-	4	-	12	3	-	0	21	0
3 – HPA	1	22	-	22	6	3	7	-	-	0	0
3 – HPA	6	20	-	25	7	0.1	8	-	-	0.1	0.5
Glycolic acid	1	77	-	0	-	0	0	-	-	-	-
Glycolic acid	6	74	-	0.1	-	0	6	-	-	-	-
Propionic acid	1	18	-	0.6	0	0	0	-	0	6	-
Propionic acid	6	25	-	3	0	0	0	-	0	4	-
α-angelica lactone	1	47	0	52	27	10	4	-	0	1	9
α-angelica lactone	6	60	4	58	23	10	4	-	0	0.3	0

The tests on malonic acid degradation showed that at high H_2O_2 concentration, the molecule presented high reactivity; in this case the conversion attested around 70 %. Malonic acid oxidized to acetic acid, which continued the pathway to glycolic acid and oxalic acid; the analysis showed an increase of around 15 % to glycolic acid and glyoxylic acid from 1 h to 6 h.

The two experiments with glycolic acid as starting material demonstrated an high reactivity of the substrate when in contact with H_2O_2 (conversion around 75 %). However, we were unable to detect any key products, due to the complete degradation to volatile compounds.

Three experiments of LEV oxidation at low loading of H_2O_2 (entries 28-30, Table 3) showed that under conditions of oxidant starvation LEV preferably converted to α-angelica lactone instead of being oxidised to succinic acid or 3-HPA. The lactone is in equilibrium with the starting material [47]. In experiments carried out starting from the lactone (Table 4), the latter was converted mainly to acetic acid and malonic acid.

3.4. The regioselectivity in Baeyer-Villiger oxidation of LEV

Results shown in Table 3 demonstrate that the H_2WO_4 controls the regioselectivity of the two competitive pathways from LEV to either succinic acid or 3-HPA. In fact, by modulating the catalyst loading we obtained a selectivity ratio succinic acid:3-HPA of > 98 %, after 6 h and at 10 % molar ratio of catalyst (Table 3, entry 27). Each increment of H_2O_2 also augmented the selectivity ratio of the two-competitive kinetics, enhancing the role of catalyst in a proportional fashion (Figure 5).

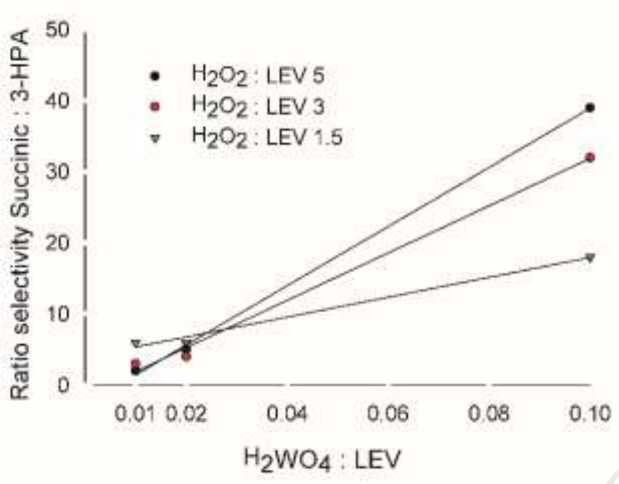

Figure 5 Direct correlation between the H_2WO_4 catalyst and the selectivity ratio succinic acid:3-HPA.

Based on these results, we propose that H_2WO_4 in an organic solvent free environment arranges with the carboxylic group of LEV to form an octagonal cyclic adduct by hydrogen bonding (Figure 6).

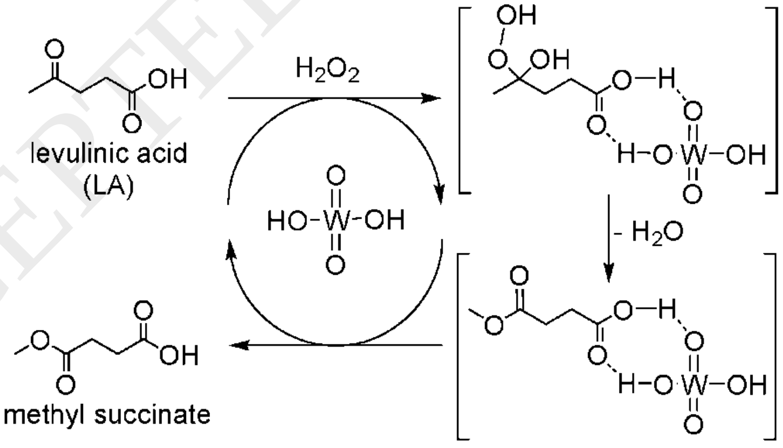

Figure 6 The H_2WO_4 catalyst interacts with LEV, forming an octagonal cyclic adduct, which due to sterical hindrance, reduced the migration of the most substituted carbon, and consequently enhances the formation of the methyl succinate

This conformation locks the molecule and impedes the Baeyer-Villiger migration of the secondary carbon by steric hindrance. Indeed, we also found that this interaction locks LEV and impedes the dehydration and the consequent cyclization to α-angelica lactone. In fact, selectivity to the lactone decreased with increasing the catalyst loading. The major example is the reduction from 38 % to 4 % lactone selectivity after 1 h reaction time, indicating the interaction of the H_2WO_4 with LEV (Table 3, entries 1 and 19).

4. Conclusions

Tungstic acid catalysed the conversion of levulinic acid to succinic acid with hydrogen peroxide and no organic solvent. We investigated the effects of time, ratio between H_2O_2 and both H_2WO_4 and the substrate. The results confirmed an interaction mechanism of the tungstic acid with the substrate, which indicates the regioselectivity of the catalyst and the decrease of LEV dehydration to α-angelica lactone. Controlling the catalyst loading modulated the selectivity of the two-competitive kinetics, achieving more than 97 % ratio between selectivities of succinic acid and 3-HPA. We achieved a maximum conversion of 48 % and 75 % selectivity to succinic acid with LEV:H_2WO_4 molar ratio of 50 and H_2O_2:LEV of 5. To investigate the decomposition pathway, we ran experiments with increasing time testing each intermediate's reactivity, with lowest amount of catalyst and a H_2O_2:LEV molar ratio of 5. We demonstrated the decomposition pathway of succinic acid, which formed acetic acid as main by-product, followed by malonic acid and formic acid.

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