

Acid-catalyzed Oxidation of Levulinate Derivatives to Succinates under Mild Conditions

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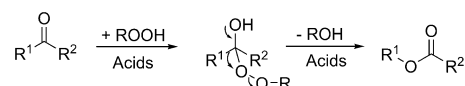
Levulinate derivatives are an attractive platform for the production of renewable chemicals. Here we report on the oxidation of methyl levulinate into dimethyl succinate with peroxides under mild conditions using Brønsted and Lewis acid catalysts. Selectivities to succinate and acetate derivatives of approximately 60 and 40%, respectively, were obtained with strong Brønsted acids in methanol. Although the molecular structure (i.e., carbon-chain length and branching around the C=O group) and the oxidant type affect the product distribution, solvent choice has the strongest impact on changing the location of oxygen insertion into the carbon backbone. Specifically, switching the solvent from methanol to heptane resulted in a decrease in the succinate/acetate ratio from 1.6 to 0.3. In contrast to Brønsted acids, we demonstrate that the nature of the metal cation is responsible for changing the reaction selectivity of water-tolerant Lewis acidic triflate salts.

The conversion of renewable resources into commodity and specialty chemicals through chemical or biological routes has attracted considerable attention.^[1] Thermocatalytic routes offer an attractive alternative to biological routes, with less stringent requirements for temperature and pH control, as well as potentially less energy-intensive product separation and purification processes.^[1a,2] Succinic acid (SA) has been identified as one of the top 12 building blocks from biomass by the US Department of Energy.^[3] The market for SA is expected to exceed \$ 1.1 billion in revenue by 2020.^[4] Succinates, formed from the esterification of SA with monoalcohols, are important plasticizers, lubricants, and chemical intermediates.^[5] A thermocatalytic route to produce SA and other succinate derivatives from renewable resources is highly desirable.

Levulinic acid (LA) is a key platform molecule that can be readily produced from lignocellulosic carbohydrates.^[6] Upon scale up, the estimated LA price is expected to decrease to less than \$ 1 kg⁻¹ from the current commercial price of approximately \$ 3.5 kg⁻¹.^[7] The carbonyl group in LA and its esters can be oxidized to produce SA and its esters, respectively;

however, linear aliphatic ketones are generally difficult to oxidize selectively. Consequently, only a few studies, mostly using vanadium-, ruthenium-, and manganese-based catalysts, have been reported on the oxidation of LA derivatives.^[8] These catalytic systems suffer from several challenges, including necessitating high reaction temperatures, using toxic reagents, or releasing a stoichiometric amount of CO₂. Recently, Podolean et al. demonstrated that Ru-based magnetic nanoparticles are efficient catalysts for the oxidation of LA into SA under 10 bar of O₂ at 150 °C.^[1b] The authors hypothesized that strong Brønsted acid sites are responsible for catalyzing the oxidation of the LA carbon backbone via a Baeyer–Villiger (BV) mechanism. Unfortunately, no systematic studies on the role of Brønsted acids in the BV oxidation of LA into SA were reported. This is particularly important given that Choudhary et al. showed that strong Brønsted acids cannot catalyze the oxidation of LA into SA with H₂O₂ in water.^[1e]

Here, we investigate the oxidation of methyl levulinate into dimethyl succinate under mild conditions using Brønsted and Lewis acid catalysts. Given the low reactivity of LA in water,^[1e] we perform our reactivity studies in solvents other than water to gain insight into the oxidation process. As shown in Scheme 1, the BV oxidation mechanism is generally accepted



Scheme 1. Acid-catalyzed oxidation of ketones using hydroperoxides via a Criegee intermediate.

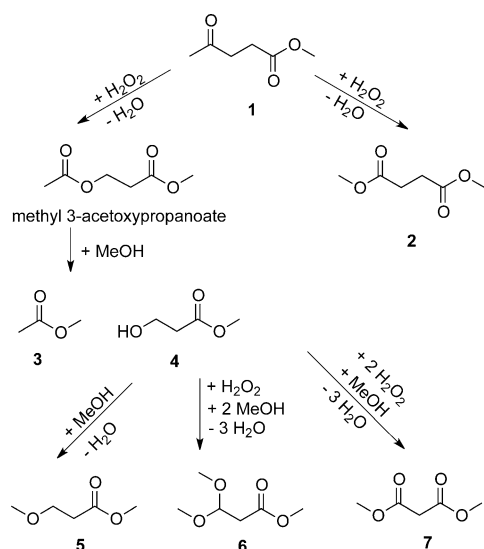
to proceed in two steps where first, a peroxide is added to a C=O group forming a Criegee intermediate, followed by migration of an R¹ group adjacent to the C=O group to insert an oxygen atom into the C–C bond in a concerted manner. Both Brønsted and Lewis acids catalyze this process by interacting with the carbonyl group, the peroxide and/or the Criegee intermediate to facilitate the addition or the migration step and influence the final product distribution.^[9]

As shown in Scheme 2, the oxidation of methyl levulinate (**1**) can follow two different pathways. For a pathway involving oxygen insertion between the δ-carbon and the γ-carbon, dimethyl succinate (**2**) is produced. Alternatively, when the oxygen insertion occurs between the γ-carbon and the β-carbon, methyl 3-acetoxypropanoate is generated, which readily hydrolyzes into methyl acetate (**3**) and 3-hydroxypropanoate (**4**) in the presence of an acid catalyst. We note that the propanoate **4** may undergo further transformation to generate methyl 3-methoxypropanoate (**5**), methyl 3,3-dimethoxypropanoate

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Scheme 2. Products obtained from the acid-catalyzed oxidation of methyl levulinate with H_2O_2 in methanol.

noate (6), and dimethyl malonate (7). Although both strong Brønsted and Lewis acids are active for the oxidation of methyl levulinate, we demonstrate that the product distribution strongly depends on the solvent polarity and, for Lewis acidic triflates, the metal cation of the triflate salt.

Shown in Table 1 are the results of the BV oxidation of methyl levulinate using both homogeneous and heterogeneous Brønsted acid catalysts with H_2O_2 as oxidant and methanol as solvent. Our data indicate that acid strength has a drastic effect on activity. Acetic acid, a weak Brønsted acid, was not active even at a levulinate/acid molar ratio of 1:1 (Table 1, entry 5). However, strong Brønsted acid catalysts, such as *p*-toluenesulfonic acid (*p*-TsOH), methanesulfonic acid (MeSO_3H), sulfuric acid (H_2SO_4), and triflic acid (TfOH), all catalyzed the levulinate oxidation effectively, generating comparable product distributions (entries 1–4). Similar conversions (defined as

Table 1. Results for the Brønsted acid-catalyzed oxidation of methyl levulinate in methanol with aqueous H_2O_2 .^[a]

Entry	Catalyst	Conv. [%]	S_M [%] ^[b]	S_A [%] ^[c]
1	<i>p</i> -TsOH	56	61	39
2	MeSO_3H	48	54	42
3	H_2SO_4	54	61	37
4	TfOH	49	61	29
5 ^[d]	CH_3COOH	<1	n.d.	n.d.
6	Amberlyst-15	13	60	36
7 ^[d]	Amberlyst-15	67	61	39
8 ^[e]	<i>p</i> -TsOH	24	55	29
9	Al-H-BEA	47	22	32

[a] Reaction conditions: methyl levulinate 61 mmol L^{-1} , levulinate/peroxide molar ratio = 1:2, levulinate/acid molar ratio = 10:1, 80°C , 6 h. [b] S_M , selectivity to succinate, moles of succinate generated/moles of levulinate converted $\times 100\%$. [c] S_A , selectivity to acetate, moles of methyl acetate generated/moles of levulinate converted $\times 100\%$. [d] Levulinate/acid molar ratio = 1:1. [e] Polymer-supported *p*-TsOH, levulinate/acid molar ratio = 9:1.

moles of substrate converted/initial moles of substrate $\times 100\%$) and selectivities (defined as moles of product generated/moles of substrate converted $\times 100\%$) obtained using *p*-TsOH, MeSO_3H , and H_2SO_4 are expected based on their similar Hammett acidity functions H_0 of ≈ 2.0 (measured in ethanol^[110,111]). For instance, *p*-TsOH converted 56% of methyl levulinate 1 after 6 h with a selectivity of 61% and 39% to dimethyl succinate 2 and methyl acetate 3, respectively (entry 1). Owing to the nature of the reaction, a concomitant 22% yield (defined as moles of product generated/initial moles of substrate $\times 100\%$) of 4 is obtained. The propanoate 4 is further converted into 6 and 7 resulting in final yields of 13 and 8%, respectively. Similar amounts of CO_2 were detected when analyzing the headspace samples of reactions using *p*-TsOH and H_2O_2 in methanol in the presence and in the absence of methyl levulinate, indicating that although terminal hydroxyl groups are readily oxidized, carbon-carbon cleavage is unlikely under the reaction conditions investigated.^[6d] Overall, the heterogeneous acids generated lower levulinate conversions compared to their homogeneous counterparts. Specifically, Amberlyst-15 and a polymer-supported *p*-TsOH material featured conversions of 13 and 24%, respectively (entries 6 and 8). Grinding the resins into powders did not increase these conversion values, but increasing the amount of catalyst from a levulinate/acid molar ratio of 10:1 to 1:1 resulted in similar conversions and product yields as those obtained with the homogeneous acids (entry 7), demonstrating that although the polymer-supported acids have lower reactivity (likely due to changes of the interaction between the acid sites and their chemical environment after immobilization),^[12] the product selectivity is not affected. Interestingly, the zeolite H-BEA generated a levulinate conversion of 47% with a succinate selectivity of 22% (entry 9), which is much lower than that obtained with the other Brønsted acids tested.

For the BV oxidation, the reported migratory aptitude of the R groups generally follows the order: tertiary alkyl > secondary alkyl > primary alkyl > methyl.^[9a,c] However, our data show that the selectivity to dimethyl succinate, the product of methyl group migration, is higher than the selectivity to methyl acetate. To rationalize this effect, we investigated the influence of the substrate's molecular structure (i.e., carbon-chain length and branching) and reaction conditions (i.e., different oxidants and solvents) on the product distribution using both a heterogeneous (i.e., Amberlyst-15) and a homogeneous (i.e., *p*-TsOH) Brønsted acid catalyst. Figure 1 shows the product distributions obtained from reacting 2-pentanone (8a), 2-hexanone (8b), and C6 methyl ketones with a branched secondary alkyl or a tertiary alkyl group (8c and 8d, respectively). In methanol with H_2O_2 as oxidant, both *p*-TsOH (red, Table S3) and Amberlyst-15 (A-15, black, Table S4) generated methyl ester 9/acetate 10 molar ratios higher than 1 for all four methyl ketones tested. Furthermore, the data show that branching of the carbon backbone also results in higher methyl ester 9/acetate 10 molar ratios. For instance, the 9d:10d molar ratio with Amberlyst-15 as the catalyst is 10.5, a value over six times as high as the molar ratio observed for 9c:10c (1.6) and about nine times as high as the one for 9b:10b (1.2). When *tert*-butyl hy-

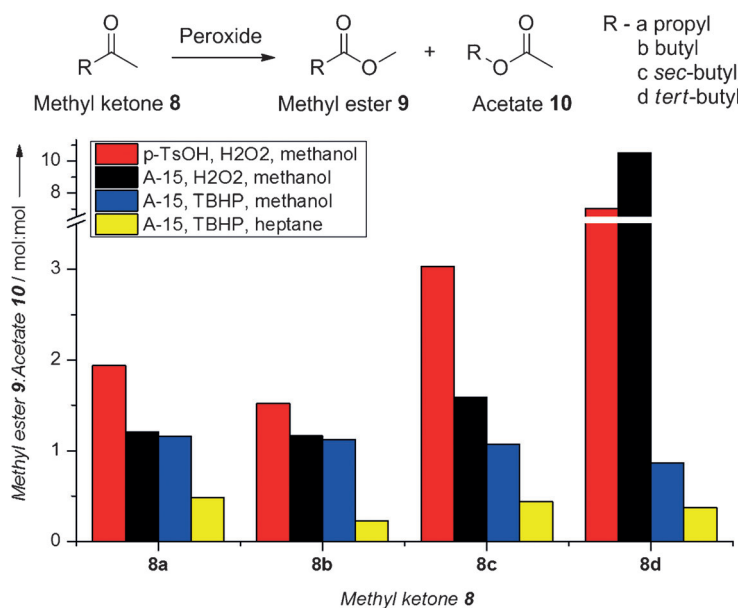


Figure 1. Product distribution for the oxidation of methyl ketones expressed as methyl ester **9**/acetate **10** molar ratios. Reaction conditions: substrate 61 mmol L⁻¹, substrate/peroxide molar ratio = 1:2, substrate/acid molar ratio = 1:1, 80 °C, 6 h, *p*-TsOH as catalyst, 50 wt% aqueous H₂O₂ as oxidant in methanol (red). Amberlyst-15 (A-15) as catalyst, 50 wt% aqueous H₂O₂ as oxidant in methanol (black). A-15 as catalyst, *tert*-butyl hydroperoxide (TBHP) in decane as oxidant in methanol (blue). A-15 as catalyst, TBHP in decane as oxidant in heptane (yellow).

droperoxide (TBHP) was used as oxidant in methanol (blue bars in Figure 1, Table S5), methyl group migration continued to dominate the product distribution under the reaction conditions investigated. However, the branched ketones yielded lower methyl ester **9**/acetate **10** molar ratios when compared to the H₂O₂ system. For instance, the **9d**:**10d** molar ratio decreased from 10.5 to 0.9 when switching to TBHP. Moreover, when the solvent was switched to heptane (yellow bars in Figure 1, Table S6), all the methyl ester **9**/acetate **10** molar ratios became lower than 1.

Evidently, the solvent choice seems to critically impact the product selectivity. With Amberlyst-15 as catalyst and TBHP in decane as oxidant, all methyl ester **9**/acetate **10** molar ratios were below 1 when heptane (yellow), instead of methanol (blue), was used as solvent. The migration ratios obtained in heptane are consistent with the general migratory aptitude for BV oxidation.^[9a,c] Selectivity shifts during the BV oxidation of aldehydes in different solvents were investigated by Lehtinen et al.^[13] Specifically, solvents capable of forming hydrogen bonds, such as methanol and 1-propanol, were shown to favor the migration of hydrogen over branched alkyl groups, while the migration of branched alkyl groups was preferentially observed in non-hydrogen-bonding solvents, such as toluene and CH₂Cl₂. Indeed, when 1-propanol and 1-butanol were used as solvents for the oxidation of **8a** and **8b**, respectively (Table S3, entries 5–6), the product distributions obtained were similar to those obtained in methanol (Table S3, entries 1–2). Considering the highly oxygenated nature of our reactive species, alcohol solvents are likely to interact strongly with the Criegee intermediate, possibly altering the stability of the transition state.

We further verified this effect by oxidizing methyl levulinate in heptane with TBHP under the same reaction conditions as those shown in Table 1. In agreement with the product distribution changes shown in Figure 1, a lower selectivity of 14% to dimethyl succinate was obtained (Table S6, entry 5).

We observe that different oxidants also affect the migratory preferences during BV oxidation. With Amberlyst-15 in methanol, aqueous H₂O₂ (black) generated higher methyl ester **9**/acetate **10** ratios than TBHP (blue), indicating the methyl migration is less favorable with TBHP as oxidant. Hawthorne et al. showed a higher differentiation of the migration groups with peroxyacetic acid as oxidant when compared to trifluoroperacetic acid for the BV oxidation of cyclohexyl phenyl ketone.^[14] It was hypothesized that the impact of the migrating groups on the energy barrier is larger for the less reactive intermediate.^[14] In our case, the different electronic and steric effects between TBHP and H₂O₂ may be responsible for the different product selectivities observed.

As a consequence, we observe that the molecular structure of the ketones, i.e., carbon-chain length and branching, also affects the migration preference. In methanol with H₂O₂ as oxidant, a higher degree of branching in the carbon backbone resulted in higher methyl ester **9**/acetate **10** molar ratios (Figure 1, red and black bars). Although in methanol with TBHP as oxidant the trend was reversed (Figure 1, blue bars), the ratios of **9a**:**10a** (C5) were higher than those of **9b**:**10b** (C6) under all the reaction conditions investigated. To our knowledge, virtually no studies exist for the BV oxidation of asymmetric ketones in alcohol solvents. Our data indicate that the migratory aptitude trend obtained in methanol is opposite to that in heptane. Mora-Diez et al. showed that the polarity of solvents affects the reaction mechanism.^[15] Hence, the available studies on BV oxidation provide limited guidance to understand the effects of oxidants, catalysts, and the molecular structure on the reaction selectivity in alcohol solvents. Future work in our group is centering on obtaining a fundamental understanding of these phenomena by way of coupled theoretical and experimental investigations.

Lewis acids are known to catalyze BV oxidations.^[9] Some metal triflates have been shown to maintain their Lewis acid activity in the presence of water, which allows their use with aqueous solutions of H₂O₂.^[16] Table 2 shows the activity of metal triflates for the oxidation of methyl levulinate. Compared to Brønsted acids, metal triflates generate lower levulinate conversions and yield a wider spectrum of product selectivities. Among the metal triflates tested, Zn(OTf)₂ showed the lowest conversion (7%) with no significant succinate formation after 6 h (Table 2, entry 11). Increasing the reaction time to 24 h resulted in a dimethyl succinate yield of 14%. The highest levulinate conversions were obtained with Hf(OTf)₄ (36%), Hg(OTf)₂ (40%), and Sc(OTf)₃ (38%), generating selectivities to succinates exceeding 47% with the rest of the carbon ending up in

Table 2. Metal triflates for methyl levulinate oxidation in methanol with aqueous H₂O₂ as oxidant.^[a]

Entry	Catalyst	Conv. [%]	S _M [%]	S _A [%]	S _M /S _A	pK _h ^[b]	WERC ^[c]
1	Hf(OTf) ₄	36	57	39	1.5	0.25	–
2 ^[d]	Hf(OTf) ₄	25	61	38	1.6	0.25	–
3 ^[e]	Hf(OTf) ₄	15	61	39	1.6	0.25	–
4 ^[f]	Hf(OTf) ₄	< 1	n.d.	n.d.	–	0.25	–
5	Hg(OTf) ₂	40	47	48	1.0	3.4	2.0 × 10 ⁹
6	In(OTf) ₃	16	26	70	0.4	4.0	4.0 × 10 ⁴
7	Sc(OTf) ₃	38	50	33	1.5	4.3	4.8 × 10 ⁷
8	Y(OTf) ₃	17	39	22	1.8	7.7	1.3 × 10 ⁷
9	Yb(OTf) ₃	16	44	21	2.1	7.7	8.0 × 10 ⁷
10	Er(OTf) ₃	16	43	31	1.4	7.9	1.4 × 10 ⁸
11	Zn(OTf) ₂	7	n.d.	41	–	9.0	5.0 × 10 ⁸

[a] Reaction conditions: methyl levulinate 61 mmol L⁻¹, levulinate/peroxide molar ratio = 1:2, levulinate/cat. molar ratio = 10:1, 80 °C, 6 h. S_M, S_A same as in Table 1. [b] pK_h = -log(K_h), K_h is the hydrolysis constant of the metal triflate.^[16b] [c] WERC, water exchange rate constant of the metal triflate.^[16b] [d] DTBP/Hf(OTf)₄ molar ratio = 0.5. [e] DTBP/Hf(OTf)₄ molar ratio = 1.4. [f] DTBP/Hf(OTf)₄ molar ratio = 4.0.

acetate-derived products (entries 1, 5, and 7). In comparison, triflates based on Y, Yb, and Er showed lower levulinate conversions of ≈ 16% with succinate selectivities of ≈ 40% (entries 8–10). Interestingly, In(OTf)₃ showed the highest selectivity to methyl acetate (70%) at a levulinate conversion of 16% (entry 6). Moreover, Group IIIB and IVB metal cations showed higher selectivities to dimethyl succinate than to methyl acetate (entries 1–3, 7–10), whereas Group IIB and IIIA metal cations showed higher selectivities to methyl acetate (entries 5, 6, and 11).

The catalytic activity of metal triflates can be correlated with their hydrolysis constant K_h and water exchange rate constant (WERC, defined as the exchange rate for substitution of inner-sphere water ligands). A lower pK_h value translates to a stronger hydrolysis tendency of the metal salt.^[16b] As such, Zn(OTf)₂ possessing the highest pK_h value (9.0), showed the lowest levulinate conversion. Similarly, triflate salts of Yb, Er, and Y, featuring pK_h values ranging from 7.7 to 7.9, showed moderate activities. For salts with pK_h lower than 4.3, including Hf(OTf)₄, Sc(OTf)₃, and Hg(OTf)₂, higher levulinate conversions were obtained. Although In(OTf)₃ has a pK_h of 4.0, it converted only 16% of the substrate (Table 2, entry 6). Unlike other triflates, In(OTf)₃ has a WERC that is orders of magnitude smaller. Given that the dissociation rate of the triflate ligand is proportional to the WERC,^[17] a smaller WERC value translates into a slower dissociation rate of the triflate ligand into triflic acid. The higher activity associated with metal triflates that possess higher dissociation and exchange constants provides strong evidence that the hydrolysis product, TfOH, is likely the true catalyst. This hypothesis was further confirmed by adding 2,6-di-*tert*-butylpyridine (DTBP), a steric hindered base,^[18] to the reaction vessel at different molar ratios (Table 2, entries 2–4). As expected, addition of DTBP progressively suppressed reactivity, up to complete deactivation upon reaching a DTBP/Hf(OTf)₄ molar ratio of 4.

The different migration preferences obtained with triflates of different groups of metals indicate a possible synergetic effect

between the metal triflate and triflic acid formed in situ that impacts product selectivity. The apparent cooperative effect between the Lewis acid centers and the generated Brønsted acid species of metal triflates has often been reported to improve the reaction activity and/or alter the selectivity in reactions, such as the etherification of glycerol with short chain alkyl alcohols and hydrothiolation of non-activated olefins.^[18a, 19] Further investigations are currently underway to understand the origins of this effect.

In summary, the oxidation of methyl levulinate into dimethyl succinate was performed using peroxide-based oxidants. Both Brønsted and Lewis acids catalyzed the reaction without significant CO₂ formation. With strong Brønsted acids, a selectivity of ≈ 60% to dimethyl succinate was obtained. Upon switching from methanol to heptane as the solvent, the selectivity decreased to 14%, indicating the strong solvent effect on directing product selectivity. Lewis acidic metal triflates generated a broader spectrum of product selectivities in methanol, which is dictated by the nature of the metal cations in the triflate salt.

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Keywords: biomass • Brønsted acids • levulinic acid derivatives • oxidation • solvent effects

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