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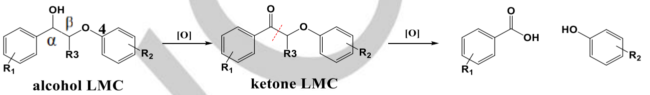
Metal Catalyst-Free Oxidative C−C Bond Cleavage of a Lignin Model Compound by H_2O_2 in Formic acid

Xiukai Li*[a] and Yugen Zhang*[a]

Abstract: Selective cleavage of the β-O-4 ether bond of lignin to produce aromatics is one of the most important topics of the sustainable production of chemicals from biomass. We demonstrate a simple system for $C_α$-$C_β$ bond cleavage of a β-O-4 ketone structured lignin model compound (LMC) by H_2O_2 in formic acid under metal catalyst-free conditions. In the system simply with H_2O_2, formic acid, and mineral acid catalyst, over 90% of product yield could be achieved in 6 h at room temperature. The reaction proceeds through the classic Baeyer-Villiger oxidation (BVO) and the *in situ* generated performic acid is the key oxidant. The cleavage of alcohol LMC by the present method in a two-step process is also successfully demonstrated.

Due to the increasing concerns on energy security and environment pollution in the recent years, there have been particular interests for the sustainable production of chemicals and fuels from renewable biomass.[1] Non-edible lignin, the second most abundant biomass in nature, is the largest source of aromatics in world.[2] For lignin, the β-O-4 ether bond is the most abundant linkage (> 50% in total) in its polymeric structure (**Scheme 1**).[3] It would be significant to depolymerise these sustainable lignin materials into aromatics or other small molecule chemicals.[4] However, because of the complex structure of lignin and the rather stable chemical bonds, only limited selectivity and yield were achieved from raw lignin. Efficient methods for β-O-4 ether bond breaking and C-C bond breaking are nessisary for lignin utilization. In this context, β-O-4 lignin model compounds (LMCs) have been widely studied for better understanding of the chemistry and challenges of real lignin.

Oxidation is one of the most important chemistry for lignin depolymerisation. Systems with catalysts like organometallics,[5] simple metal irons,[6] and metal oxides[7] have been developed for oxidative lignin depolymerisation or LMCs cleavage, resulting in poor to good product yields. The breaking of the β-O-4 ether bond could happen at $C_α$-$C_β$ or $C_β$-O bonds. Generally, the $C_α$-$C_β$ bond is more difficult to be cleaved than the $C_β$-O bond due to the higher energy barrier.[8] Oxidation of $C_α$-OH to ketone is of particular significance for LMCs cleavage.[9] Computational and experimental studies indicate that the β-O-4 ether bond shows higher tendency to be cleaved when the $C_α$-OH was oxidized to ketone.[9a, 10] When the $C_α$-OH was oxidized to ketone, the dissociation energy for the $C_β$-O bond reduced from 69.2 kcal mol^{-1} to 55.9 kcal mol^{-1}.[10] Various oxidation methods have therefore been developed for the transformation of the β-O-4 alcohol LMC to the β-O-4 ketone LMC,[8b, 9, 11] and over 90% product yields could be achieved.[9c, e, 11] There have also been fewer reports on tandem reactions for more difficult $C_α$-$C_β$ bond cleavage via the ketone-structured LMC (**Scheme 1**). As a good example, Wang et al.[11a] developed a two-step process for $C_α$-$C_β$ cleavage of LMC. The β-O-4 alcohol LMC was oxidized to β-O-4 ketone LMC by pressurized oxygen with the assist of $VOSO_4$/TEMPO catalysts, and then cleaved by pressurized oxygen in presence of organometallic Cu complex.



Scheme 1. Two-step strategy for $C_α$-$C_β$ cleavage of β-O-4 alcohol LMC via the β-O-4 ketone LMC.

Baeyer-Villiger oxidation (BVO) by peroxides is a classic method to form an ester from a ketone. Inserting an oxygen atom to LMC substrate by BVO would enable easier dissociation of the inert $C_α$-$C_β$ bond of β-O-4 LMC. In 2013, Stahl et al.[11b] demonstrated the cleavage of $C_α$-$C_β$ bond of ketone LMC by H_2O_2 under basic condition (2 M NaOH) in THF/methanol (1/1) mixed solution. Veratric acid in 88% yield and guaiacol in 42% yield was achieved from this system. In 2017, Zhang et al.[8a] used sole 3-chloroperbenzoic acid or H_2O_2 in combination with $(PhCH_2Se)_2$ catalyst for Baeyer-Villiger oxidation of ketone LMC. The acetal ester and aryl ester products from BVO were further dissociated by alcoholysis in K_2CO_3/alcohol mixture. The breakthrough of previous work inspired us to look for a simpler system for $C_α$-$C_β$ bond cleavage of β-O-4 LMC. In this work, ketone LMC was cleaved directly by H_2O_2, a green and liquid oxidant,[12] in formic acid under metal catalyst-free conditions, and over 85% product yield was achieved in 4 h at 100 °C. With mimeral acid catalyst, the reaction was efficient at room temperature (25 °C) and over 90% of product yield could be achieved in 6 h.

In view that the selective oxidations of β-O-4 alcohol LMC to ketone LMC have been well documented and high product yields could be achieved,[8b, 9, 11a] a ketone-structured LMC, 2-phenoxy-1-phenylethanone **(1),** was employed as substrate directly in our work. In our initial study, we tried to cleave **(1)** directly by H_2O_2 in various solvents without addition of any acid, base, or metal catalyst (Table 1). Over 90% conversions were achieved in C1 ~ C4 organic acids (Entries 1 ~ 4, Table 1) in 4 h at 100 °C. The conversions were dropped to less than 10% when other solvents were used, (Entries 5 ~ 8, Table 1). Phenoxymethyl benzoate **(2)**, benzoic acid **(3)**, and phenol **(4)** were the major products for all solvents. Phenyl formate and benzaldehyde were produced in < 1% yield, thus, they were not included in Table 1. Some unidentified products were also detected in our GC analysis. With increasing length of the carbon chain of acid, the yield for **(2)** increased while the yields for **(3)** and **(4)** decreased. In formic acid solvent, full conversion was achieved with 85.9% yield for **(3)** and 18.4% yield for **(4)**. In butyric acid solvent, **(2)** was produced at

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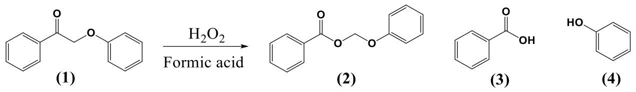
61.8% yield while **(3)** and **(4)** were produced at the yields of 17.8% and 1.9%, respectively. The changes in conversions and product yields with respect to different solvents signify that organic acids play profound roles in ketone LMC cleavage by H_2O_2.

Table 1. Oxidative cleavage of lignin model compound **(1)** in different solvents.



Entry	Solvent	Conv. / %	Yield / %		
			(2)	(3)	(4)
1	formic acid	100.0	0.0	85.9	18.4
2	acetic acid	93.2	48.0	30.8	8.7
3	propionic acid	99.0	54.3	31.0	1.4
4	butyric acid	97.8	61.8	17.8	1.9
5	DMSO	9.9	0.0	4.8	8.1
6	*t*-butanol	6.4	1.8	6.1	8.1
7	IBMK	3.8	0.4	0.0	7.4
8	H_2O	< 1.0	0.0	0.0	0.0

Reaction conditions: 2-phenoxy-1-phenylethanone **(1)**: 107 mg (0.5 mmol), H_2O_2 (31%): 0.5 mL, solvent 2 mL, 100 °C, 4 h.

As high conversion and good product yields were achieved for **(1)** cleavage in formic acid, the amount of formic acid and other variables such as reaction temperature, reaction time, and amount of H_2O_2 were further studied. Figure 1A shows that the amount of formic acid had a significant influence on the reaction. The conversion of **(1)** and the yield for **(3)** increased with increasing amount of formic acid. Over 90% conversion for **(1)** and over 80% yield for **(3)** were achieved when the amount of formic acid exceeded 1 mL. However, in a comparison reaction with 1 mL of formic acid plus 1 mL of DMSO as solvent, the conversion of **(1)** was less than 5%. Thus, it is concluded that high concentration of formic acid is essential for this reaction. Figure 1B shows the effect of reaction temperature on the reaction. Though over 90% conversion was achieved in 4 h at room temperature (25 °C), the dominant product was acetal ester **(2)** at 69.1% yield and the cleavage products were at respectively 18.2% yield for **(3)** and 7.3% yield for **(4)**. With temperature rise, the yield for **(2)** decreased drastically, and the yield for **(3)** increased accordingly and reached 85.9% at 100 °C. Further increase in temperature did not affect the conversion and yields for **(3)** and **(4)** significantly. The optimal reaction time at 100 °C was 4 h and the optimal loading amount of H_2O_2 was 0.5 mL (Figures S1). The reaction performed at room temperature was slower but would be helpful to understand the reaction mechanim and the evolution of products. Figure 1C demonstrates that the conversion increased quickly to 92.2% in the first 4 h at room temperature (25 °C). The yield for **(2)** reached 69.1% in 4 h and then decreased gradually at prolonged reaction time. The yield for **(3)** increased continuously and reached 53.9% in 65 h. The yield for **(4)** was always less than 10% due to the formation of side products. The reverse trends in yields for **(2)** and **(3)** signify that **(2)** is an intermediate for the reaction and that the transition of **(2)** to **(3)** is kinetic controlled.

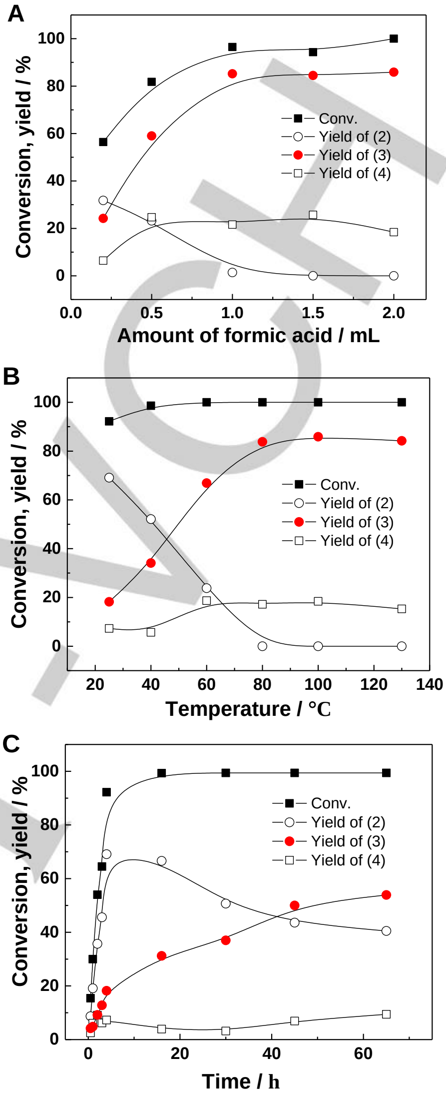


Figure 1. (A) Lignin model compound **(1)** cleavage by H_2O_2 in different amount of formic acid at 100 °C for 4 h, (B) Lignin model compound **(1)** cleavage by H_2O_2 in 2 mL formic acid for 4 h at different reaction temperatures, and (C) lignin model compound **(1)** cleavage by H_2O_2 in 2 mL formic acid for different reaction time at room temperature (25 °C). Other reaction conditions: substrate **(1)** 107 mg (0.5 mmol), H_2O_2 (31%) 0.5 mL.

The results in Figure 1 suggest that the cleavage of **(1)** by H_2O_2 is efficient in organic acids such as formic acid; however, the reaction was sluggish in other types of solvents as have been reported in Table 1. Thus, the reaction in formic acid was monitored by NMR (Figure 2) to better understand the roles of this particular solvent. Blank experiment show that there was no reaction happened between LMC **(1)** and formic acid in the absence of H_2O_2 (Figure 2 a). In the LMC **(1)**/H_2O_2/formic acid system (Figure 2, b ~ f), new signal (δ 8.21) attributable to performic acid in addition to that of formic acid (δ 7.99) was observed. The -CH_2- signal (δ 5.30) for substrate **(1)** diminished gradually with time while the -CH_2- signal (δ 5.83) for **(2)** increased accordingly. In Table 1, it has been shown that the reaction cannot proceed in aquous H_2O_2 probably because of the poor solubility of the substrate. However, in homogeneous DMSO and *t*-butanol systems (Entries 5 & 6, Table 1), the conversions of **(1)** by H_2O_2 were still much lower (< 10%). Thus, it is concluded that the *in situ* generated performic acid in stead of H_2O_2 should be the oxidation species for this reaction. Based on the results of kinetic study and NMR analysis, we propose the reaction should follow the classic Baeyer-Villiger oxidation mechanism (Scheme 2): performic acid attacks the carbonyl group of **(1)** to form the Criegee intermediate, then to acetal ester **(2)**; the dissociation of **(2)** leads to benzoic acid **(3)** and phenol **(4)**. Organic peracids have stronger -O-O- bonds than H_2O_2 because of the electron-withdrawing effect of the carbonyl group.[13] Moreover, the organic acids and peracids provide strong acidic environments that are favorable for the BVO and the dissocaition of the intermediate product **(2)**. With increasing length of the carbon chain, the acidity of organic acid decreases and the dissociation of the intermediate becomes slower as have been shown in Table 1. Similar effects of organic acid on BVO have also been observed in our previous study on furfural oxidation to maleic acid by H_2O_2.[13] Using *in situ* generated perorganic acids as oxidants is a method for biomass varitization, however, the extents of oxidations and the selectivities for products depend significantly on the type and concentration of the organic acid employed in the reaction.[13-14]

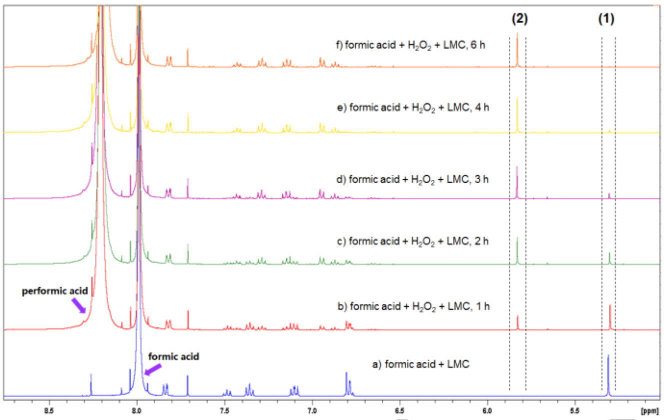
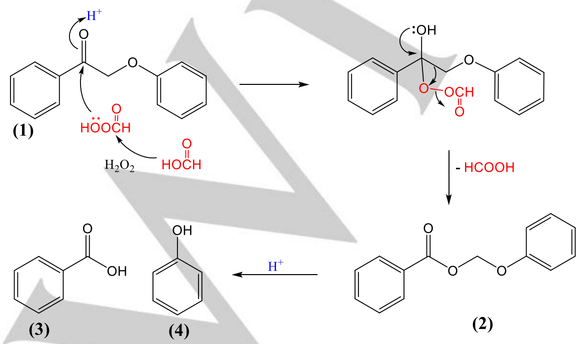


Figure 2. Lignin model compound LMC **(1)** cleavage by H_2O_2 in formic acid at room temperature (25 °C) in the absence of H_2O_2 (a) and in the presence of H_2O_2 (b ~ f). Substrate **(1)** 107 mg (0.5 mmol), H_2O_2 0.5 mL, formic acid 2 mL.



Scheme 2. The proposed reaction mechanism for lignin model compound **(1)** cleavage by *in situ* generated performic acid.

The reaction conducted at room temperature would be energy efficient. The results in Figure 1 show that the BVO of ketone LMC **(1)** to **(2)** by performic acid is efficient in a broad range of temperature, however the dissociation of the intermediate **(2)** to **(3)** and **(4)** was kinetic controlled and slow at room temperature. Inspired by the result that the reaction was faster in the stronger formic acid solvent than in other weaker organic acids (Table 1), various mineral acids with different strength was added into the system to accelerate the reaction at room temperature. The amounts of H^+ were 0.1 mmol for all added acids. From Table 2, it can be seen that the dissociation of **(2)** is correlated with the strength of the acid additive. With the strongest F_3CSO_3H and $HOCl_4$ acids, respectively 96.3% and 86.2% yields for **(3)** were achieved and less than 2% for **(2)** was remained. With medium strength H_2SO_4 added, the yield for **(3)** increased to 62.6% and the yield for **(2)** dropped to 21.4%. When acids with lower strength such as HNO_3, H_3PO_4, and solid Amberlyst-15 were used, the yield for **(2)** decreased by less than 10%. When hydrochloric acid was used as an additive, the conversion was still high but the selectivities for products were low and a lot of side products were observed. This is probably because hydrochloric acid was destroyed in the strong oxidizing environment. Thus, a strong protonic acid is favorable to catalyze the conversion of **(1)** to **(3)** at room temperature.

Table 2. Oxidative cleavage of lignin model compound **(1)** by H_2O_2 in formic acid with mineral acid additives at room temperature.

Entry	Acid additive (concentration)	Conv. %	Yield %		
			(2)	**(3)**	**(4)**
1	-	92.2	69.1	18.2	7.3
2	F_3CSO_3H (98%)	99.5	0.5	96.3	28.9
3	$HOCl_4$ (70%)	98.6	1.7	86.2	35.4
4	H_2SO_4 (98%)	94.8	21.4	62.6	35.2
5	HNO_3 (65%)	96.1	65.2	27.3	11.0
6	H_3PO_4 (85%)	96.1	61.6	28.8	12.0
7	HCl (37%)	98.1	28.9	20.1	2.2
8	Amberlyst-15	94.6	66.0	20.6	8.0

Reaction conditions: substrate **(1)** 107 mg (0.5 mmol), H_2O_2 (31%) 0.5 ml, acid additive 0.1 mmol of H^+, formic acid 2 mL, 25 °C, 4 h.

H_2SO_4 is safer and cheaper than F_3CSO_3H and $HOCl_4$, therefore, more applicable in large scale synthesis. The loading amount and the reaction time for H_2SO_4 as a catalyst were further optimized. As depicted in Figure 3A, the yield for **(3)** increased with increasing loading amount of H_2SO_4. Over 80% of **(3)** was produced when the amount of loaded H_2SO_4 exceeded 30 µL (0.15 mmol). With 30 µL of H_2SO_4 added (Figure 3B), the yield for **(3)** increased continuously with time and reached 94.4% in 8 h. There was an optimal reaction time for phenol **(4)**. The 43.5% yield of **(4)** maximized at 2 h, then started to decrease at longer reaction time. Thus, under optimized conditions with H_2SO_4 as a catalyst, product yields could be achieved comparable to that from the cases with strong F_3CSO_3H and $HOCl_4$ as catalysts.

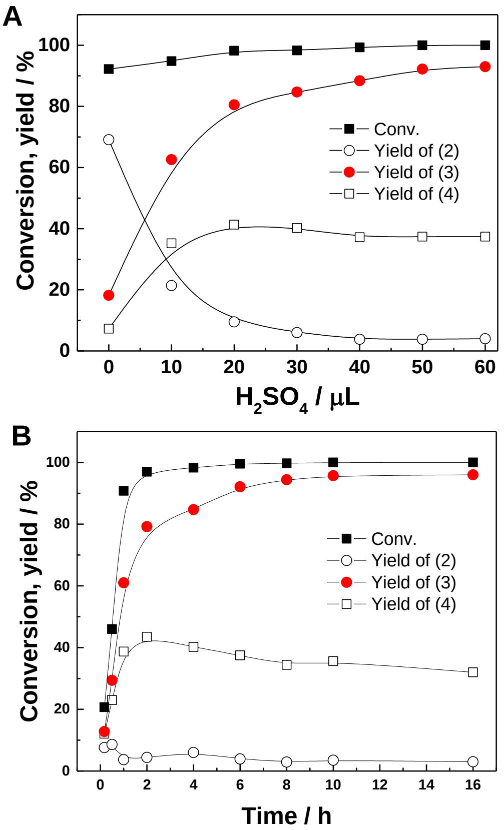


Figure 3. (A) Lignin model compound **(1)** cleavage by H_2O_2 in formic acid with different amount of H_2SO_4 for 4 h at room temperature (25 °C), and (B) Lignin model compound **(1)** cleavage by H_2O_2 in formic acid with 30 µL of H_2SO_4 at room temperature (25 °C). Other reaction conditions: substrate **(1)** 107 mg (0.5 mmol), H_2O_2 (31%) 0.5 mL, formic acid 2 mL.

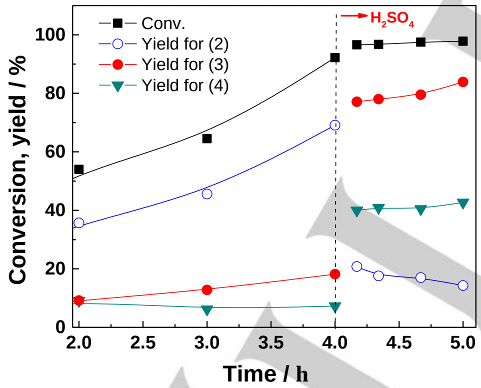
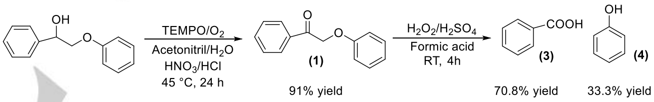


Figure 4. Lignin model compound **(1)** cleavage by H_2O_2 in formic acid. H_2SO_4 (30 µL) was added 4 h after starting the reaction. Reaction conditions: substrate **(1)** 107 mg (0.5 mmol), H_2O_2 (31%) 0.5 mL, formic acid 2 mL, room temperature (25 °C).

To further clarify the role of proton in each step of **(1)** oxidative cleavage to **(3)** and **(4)** by H_2O_2, we added H_2SO_4 at the reaction time 4 hours after starting the reaction (Figure 4). About 92.2% conversion of **(1)** was attained in 4 h at room temperature without any mineral acid added, and the yields for **(2)**, **(3)**, and **(4)** were 69.1%, 18.2% and 7.3%, respectively. In 10 min after 30 µL of H_2SO_4 was added, the yield for **(2)** dropped from 69.1% to 20.8% while the yield for **(3)** and **(4)** increased rapidly from 18.2% to 77.1% and 7.3% to 40.0%. It is clear that **(2)** dissociation to **(3)** is the rate-limiting step in the whole process. A weak acid is able to catalyze the conversion of **(1)** to **(2)**, but a strong acid is required for the dissociation of **(2)** to **(3)** and **(4)**. The strong acid additive could be added at the initial stage or several hours after starting the reaction. Raising the reaction temperature is another method to promote this rate-limiting step as that has been shown in Figure 1.

Methoxy group is the most common substituent at the aromatic rings in lignin. For a β-O-4 model compound with the methoxy group at the ortho- position of phenoxy part (LMC3), up to 93.8% yield for benzoic acid and 20.2% yield for 2-methoxy phenol were achieved with full conversion at room temperature for 16 h (Table S1). However, for a model compound with methoxy groups at the meta- and oposite- positions of the phenylethanone part (LMC4), the reaction was sluggish which is due to the electron-donating nature of the CH_3O- group and affects the nucleophile attack of performic acid to ketone.

The results for ketone LMC cleavage by BVO in simple H_2O_2/formic acid/H_2SO_4 system is encouraging. Since alcohol lignin is prevalent in natural than the ketone lignin, we further demonstrated the conversion of alcohol LMC by our method. The direct cleavage of the alcohol LMC in the typical H_2O_2/formic acid/H_2SO_4 system resulted in high conversion but broad product distribution from **(1)**, **(3)**, and **(4)** to other side products. Thus, we developed the two-step reaction route as illustrated in Scheme 3. In the first step, alcohol LMC was oxidized by TMPO/O_2 in acetonitrile/H_2O solvent[11b] and 91% yield for ketone LMC was achieved in 24 h at 45 °C. With crude ketone LMC for the second step reaction, 70.8% yield for **(3)** and 33.3% yield for **(4)** were obtained in 4 h at room temperature from the H_2O_2/formic acid/H_2SO_4 system in this single step. These results provide additional support for the two-step lignin conversion strategy proposed in Scheme 1.



Scheme 3. The two-step strategy for alcohol LMC cleavage via the ketone LMC intermediate. Step 1: alcohol LMC 107 mg (0.5 mmol), TEMPO 10 mg, O_2 50 psi, acetonitrile 2.5 mL, H_2O 130 µL, HNO_3 (65%) 5 µL, HCl (37%) 5 µL, 45 °C, 24 h. Step 2: crude LMC **(1)** from previous step, H_2O_2 (31%) 0.5 mL, formic acid 2 mL, H_2SO_4 (30 µL), room temperature (25 °C), 4 h.

In summary, we have demonstrated a very simple system for C-C cleavage of ketone LMC by Baeyer-Villiger oxidation (BVO) under metal catalyst-free conditions. In the system with ketone LMC, H_2O_2 and formic acid reagents, over 85% product yield was achieved in 4 h at 100 °C. Catalytic ammount of mineral acids could accelerate the reaction and over 90% of product yield could be achieved in 6 h at room temperature (25 °C). Mechanic study indicated that the *in situ* generated performic acid is responsible for the BVO of ketone LMC. Strong mineral acids accelerate the dissociation of the acetal ester intermediate to form small molecule aromatics. The cleavage of alcohol LMC by the present method was also demonstrated in a two-step reaction process.

Experimental Section

Lignin model compounds synthesis. 2-phenoxy-1-phenylethanone (LMC **(1)**) and 2-phenoxy-1-phenylethanol (LMC **(2)**) were synthesized

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according to previous report with phenol and 2-bromoacetophenone as the starting materials.[4h]

Oxidative cleavage of LMC (1).LMC **(1)** (107 mg, 0.5 mmol), formic acid (2 mL), H_2O_2 (0.5 mL), and H_2SO_4 (concentrated (98%), 30 µL) were charged into a thick wall glass vial (8 mL). The vial was sealed and stirred at room temperature (25 °C) for 4 h. The sample containing known amount of mesitylene as an internal standard was analysed by Agilent GC6890N with FID and capillary column (HP FFAP, 30 m × 0.32 mm, 0.25 µm).

Isolation of the intermediate product (2). LMC **(1)** (424 mg, 2 mmol), formic acid (8 mL), and H_2O_2 (2 mL) were charged into a thick wall glass vial (16 mL). The vial was sealed and stirred at room temperature (25 °C) for 4 h. After that, 20 mL of water was added. The products were extracted with 20 mL of Et_2O. A light yellow liquid was obtained after Et_2O was removed by evaporation. Phenoxymethyl benzoate (the intermediate) was separated at 50% yield by flush column with hexane/ethyl acetate = 32/1 (v/v) as the mobile phase.

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Keywords: biomass • oxidation • lignin • formic acid • hydrogen peroxide

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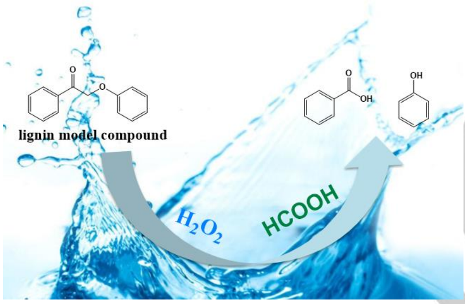
COMMUNICATION

In the system simply with H_2O_2, formic acid, and mineral acid catalyst, over 90% of product yield could be achieved from C_α-C_β bond cleavage of a β-O-4 ketone structured lignin model compound in 6 h at room temperature.



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Metal Catalyst-Free Oxidative C−C Bond Cleavage of a Lignin Model Compound by H_2O_2 in Formic acid