Free radical reaction promoted by ionic liquid: a route for metal-free oxidation depolymerization of lignin model compound and lignin

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References

1. General

Tert-butanol (>99.5%), methyl tertiary butyl ether(>99%), tetrahydrofuran(A.R.), diethyl ether(A.R.), NH_4Cl(A.R.), NaCl(A.R.) were obtained from Sinopharm Chemical Reagent Co., Ltd.. Phenol(99%), potassium carbonate(K_2CO_3, 99%), 2-Bromoacetophenone(99%), diphenyl ether(99%), benzyl phenyl ether(99%), sodium borohydride(98%) were purchased from Alfa Aesar. Acetonitrile(CH_3CN), toluene, phosphoric acid (H_3PO_4, 85% aqueous solution) were obtained from the Beijing Chemical Company. Organosolv lignin was provided by Beijing Forestry University. 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BnMIm][NTf_2], 99%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIm][NTf_2], 99%), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIm][NTf_2], 99%), 1-butyl-3-methylimidazolium chloride([BMIm]Cl, 99%), 1-butyl-3-methylimidazolium hydrosulfate([BMIm][HSO_4], 99%), 1-hexyl-3-methylimidazolium dihydrophosphate([HMIm][H_2PO_4], 99%), were purchased from Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. All the ionic liquids were dried at 70 ^{o}C for 24 hours before used.
Oxygen(>99.99%), nitrogen(>99.99%), hydrogen(>99.99%), carbon monoxide (>99.99%) and carbon dioxide(>99.99%) were provided by Beijing Analytic Instrument Company.

2. Preparation of 2-phenoxyacetophenone(1) and 2-phenyloxy-1-phenylethanol

Experimental procedure: **1** was synthesized according to the procedures reported in literature. [1] In the experiment, a three-neck round bottom flask equipped with a reflux condenser was charged with 5.2 g phenol (55 mmol), 13.88 g potassium carbonate (100 mmol), and 100 mL acetonitrile. The flask was heated to reflux temperature, and then 10 g of 2-bromoacetophenone (50 mmol) dissolved in 50 mL acetonitrile was added dropwisely into the flask. The mixtures were stirred for 4 hour at reflux temperature, and then it was filtered through Celite and concentrated in vacuo. The resulting solid was purified by column chromatography to abtain **1**. NMR spectra were acquired on a Bruker Advanve III-400HD spectrometer. NMR chemical shifts are reported as δ in parts per million (ppm) relative to the residual solvent signal. ^{1}H NMR ($CDCl_3$, 400MHz)[ppm] δ 8.003-8.021(d, 2H), 7.62(t, 1H), 7.5-7.52(t, 2H), 7.274-7.314(t, 2H), 6.94-7.01(m. 3H), 5.27(s, 2H).

2-Phenyloxy-1-phenylethanol was synthesized according to method in literature. [1] A round bottom flask was charged with **1** (2 g, 9.4 mmol), tetrahydrofuran(40 mL), and water (10 mL). Sodium borohydride (0.712 g, 18.8 mmol) was added portion-wise to maintain a gentle evolution of gas over 5 minutes, after which the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and then the reaction mixture was diluted with water (50 mL). The aqueous portion was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were washed twice with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give 1.8 g of 2-phenyloxy-1-phenylethanol as a white solid (90%). ^1H NMR ($CDCl_3$, 400MHz)[ppm] δ 7.452-7.473(d, 2H), 7.376-7.395(t, 2H), 7.334-7.349 (d, 1H), 7.273-7.303(t, 2H), 6.956-6.993(t, 1H), 6.914-6.934(d, 2H), 5.114-5.144(d, 1H), 4.100-4.132(d, 1H), 3.990-4.036(t, 1H).

3. Oxidation of lignin model compounds

Experimental procedures: The oxidation reactions were conducted in a Teflon-lined stainless steel reactor of 10 mL, which was similar to that used previously. [2] In the experiment, desired amount of IL, acid (e.g. H_3PO_4) aqueous solution, lignin model compound or lignin, and water were added in the reactor. The air of the reactor was removed under vacuum and the reactor was placed in the preheated furnace of the desired temperature, then oxygen was charged into the reactor and the stirrer of the reactor was started. After a suitable reaction time, the reactor was cooled in the ice water, and the gas was released into a gas sample bag. Gasoues product was analysed by GC (gas chromatography) with TCD detector. Qualitative analysis was proceeded by GC-MS with products extracted by methyl tertiary butyl ether from the liquid. Quantification of the liquid product was analysed by high performance liquid chromatography, which was performed on a SHIMADZU LC-15C series with a UV detector (at 280 nm) and a C18 column (4.6 × 250 mm). Column temperature was 308 K. Water/acetonitrile with gradient elution was used as the mobile phase. 1-18 min ($CH_3CN:H_2O=20:80$), 18-19 min (from $CH_3CN:H_2O=20:80$ to $CH_3CN:H_2O=50:50$), 19-50 min ($CH_3CN:H_2O=50:50$).

4. Oxidation of lignin model compound 1 promoted by different acids

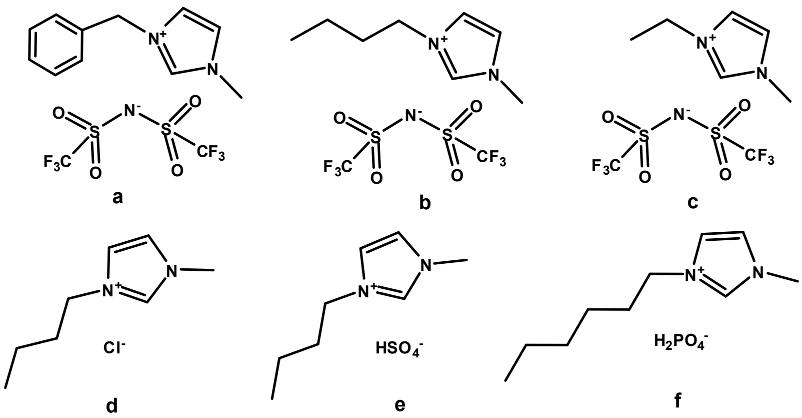
Table S1. Oxidation of lignin model compound **1** promoted by different acids.[a]

Acid	Conversion(%)	Y(**2**)(%)[b]	Y(**3**)(%)[c]
H_2SO_4	100	73	49
HCl	85	61	34
H_3PO_4	100	89	84
H_2WO_4	62	59	57
CH_3COOH	60	56	30

[a]. Reaction conditions: reactant **1** 0.212 g, IL 1 g, H_2O 46 μL, O_2 1.0 MPa, temperature 403 K, reaction time 3 hours; appropriate amounts of acids with the equivalent molar amounts of H^+ as 85% H_3PO_4.(16 μL).

[b]. Y(**2**) = Yield of benzoic acid; [c]. Y(**3**)=Yield of phenol.

5. Structures of the ILs used

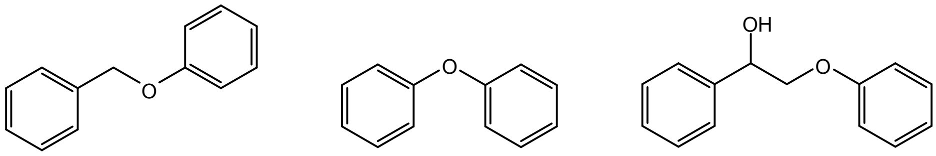


Scheme S1. Structures of the ILs used. a) [BnMIm][NTf$_2$], b) [BMIm][NTf$_2$], c) [EMIm][NTf$_2$], d) [BMIm]Cl, e) [BMIm][HSO$_4$], f) [HMIm][H$_2$PO$_4$].

6. UV-vis absorption study

The apparatus and procedures were similar to those used previously.[3] The apparatus consisted of gas cylinders (O_2, N_2), a high-pressure UV sample cell with two quartz windows, a pressure gauge, and a temperature controller. The optical path length and the inner volume of the cell were 21 mm and 6.5 mL, respectively. In a typical experiment, suitable amount of tert-butanol solution of 2-phenoxyacetophenone was loaded into the sample cell. Then O_2 (N_2) was charged to 10 bar. The absorbance spectrum was recorded by a TU-1201 Model spectrophotometer (Beijing General Instrument Company). The UV-vis absorption spectra are shown in Figure 2A.

7. Structures of other lignin model compounds


benzyl phenyl ether diphenyl ether 2-phenyloxy-1-phenylethanol

Scheme S2. Structures of other lignin model compounds.

8. EPR experiments and spectra

Measurements were performed using a Bruker ER 300 EPR spectrometer operating at X-band with a TM 110 cavity with a quartz flat cell. The microwave frequency was measured with an EIP Model 575 microwave counter (EIP Microwave, Inc., San Jose, CA). Spectra were recorded at ambient temperature (25℃).

Procedures for the generation of OOH free radical by riboflavin in [BnMIm][NTf_2]: The mixture of 1 mM riboflavin and 0.2 mM DMPO was added to [BnMIm][NTf_2]. After shaking for 1 min, the EPR experiment was carried out in sunlight as blank, and no signals were observed. Then the mixtures were irradiated by UV-light (350 nm), and the EPR spectrum was obtained as depicted in Figure S1a.

Procedures of spin trap in our reaction system: In the experiment, desired amounts of IL, 85% H_3PO_4 aqueous solution, lignin model compound, water and DMPO were added in the reactor. The air of the reactor was removed under vacuum and the reactor was placed in the preheated furnace of the desired temperature, then oxygen was charged into the reactor to 1 MPa and the stirrer of the reactor was started. After 40 min, the reactor was opened, a suitable amount of reaction solution was taken out, and the EPR spectrum was recorded. The spectra of [BnMIm][NTf_2] and [BMIm][HSO_4] reaction systems were shown in Figure 2B and Figure S1b, respectively.

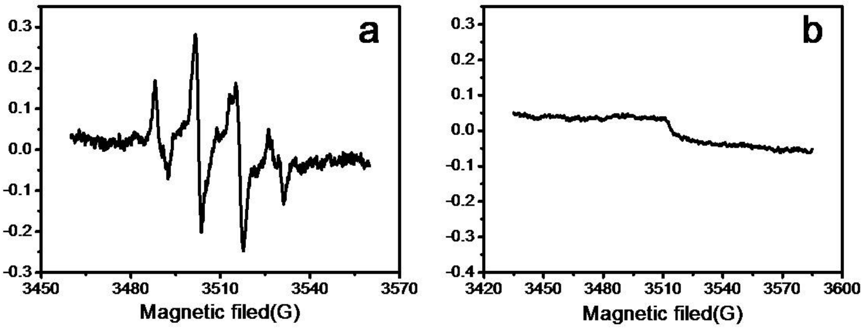


Figure S1. a) EPR spectrum of DMPO-OOH in IL ([BnMIm][NTf_2]) (g=2.06±0.002); b) EPR spectrum of DMPO-OOH in IL ([BMIm][HSO_4]).

9. GC analysis spectra of gaseous products

Figure S2 shows the GC spectra of typical gas products in the reaction. The peaks were identified by standard gases. The gaseous products collected from the reactor contained hydrogen, oxygen, carbon monoxide and carbon dioxide.

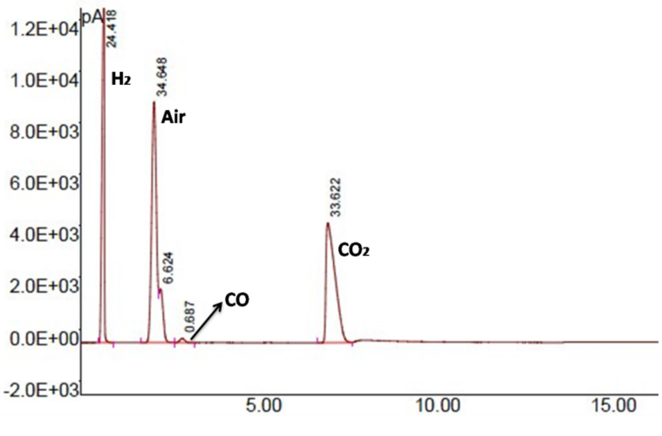


Figure S2. GC trace of the gaseous products of the reaction at the condition of entry 2 in Table 1.

10. The spectra of high performance liquid chromatography of the oxidation reaction

Figure S3 shows the spectra of typical products and reactant in the reaction. The peaks were identified by standard reagents. The substances contained formic acid, phenol, benzoic acid and 2-phenoxyacetophenone.

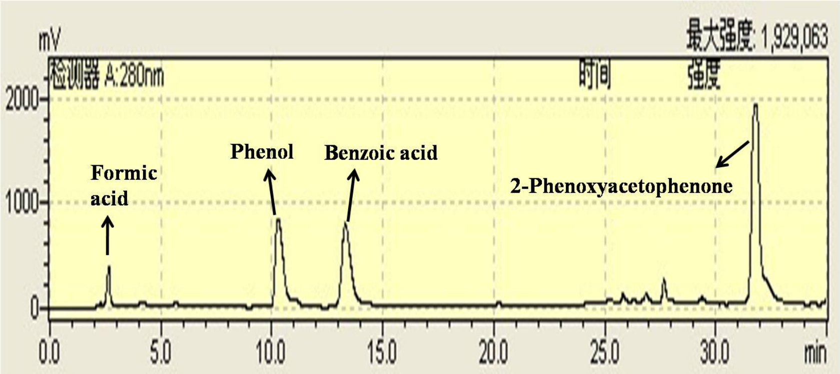


Figure S3. Spectra of high performance liquid chromatography of the oxidation reaction.

11. Reuse of [BnMIm][NTf$_2$]

After the oxidation reaction, methyl tertiary butyl ether (4×3 mL) was used to extract the product from the reaction mixture. The IL [BnMIm][NTf$_2$] was washed by water (3×5 mL), and dried in vacumm at 343 K for 24 hours. Then the IL was reused in the next run at the same reaction condition.

References

1 J. Buendia, J. Mottweiler, C. Bolm, *Chem-Eur. J.* 2011, **17**, 13877.

2 H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang, Y. X. Zhou, *Science* 2009, **326**, 1250.

3 Z. M. Xue, J. L. Zhang, L. Peng, J. S. Li, T. C. Mu, B. X. Han, G. Y. Yang, *Angew. Chem. Int. Ed.* 2012, *51*, 12325-12329.