Cleavage of the β—O—4 linkage of lignin using group 8 pincer complexes: A DFT study

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A B S T R A C T

The catalysis of C—O bond activation of the lignin β—O—4 model compound, 2-phenoloxy-1-phenolethanol, was investigated using group 8 (Fe, Ru and Os) pincer complexes. Reaction mechanisms and thermodynamics for the catalysis were studied using B3LYP/CEP-31G. Solvent effects were considered using a SMD solvation model for 1,4-dioxane. The considered pincer complexes include combinations of the three metals with five different pincer ligands (PNP, NNN, PCP, PCN and NCN). All possible multiplicities and conformations were taken into account. The reaction energetics of all metal-ligand combinations were compared and the thermodynamic nature of transition metal activation of the β—O—4 bond was discovered. The studies suggest that C—O bond activation by transition metal catalysts is essentially controlled by the ability of the metal center to donate electrons to the C—O bond; ligands that donate electrons to the metal center tend to facilitate the cleavage of the C—O bond.

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1. Introduction

Rapid decline of fossil fuel dependency on foreign sources has led to the investigation of alternative carbon feedstocks, such as biomass materials [1]. Lignin, along with cellulose and hemicelluloses, are the three major components of lignocellulosic biomass. Despite the high energy content of lignin (15 ∼ 30% by weight and 40% by energy of all the biomass components), it has received little attention compared to cellulose [2]. Nevertheless, lignin has great potential as a sustainable carbon resource for fuels and bulk chemical production [3]. The unique structure and chemical properties of lignin allow a diverse range of useful chemicals, particularly aromatic compounds, to be produced [2].

Lignin is a three-dimensional polymer of different phenylpropane units connected by C—O and C—C bonds. The direct utilization of lignin is difficult due to the complex structure. Thus the first step of processing lignin generally involves depolymerization by pyrolysis or catalytic degradation to produce low-molecular weight oxygenated compounds [4,5]. These compounds would then be upgraded using zeolite or supported hydrodeoxygenation catalysts for oxygen removal [6]. Current studies have shown that delivering valuable small feedstocks from lignin often requires pyrolysis at high temperatures between 250 and 600 °C [4]. On

the other hand, lignin degradation using effective unsupported catalysts has allowed the process under low temperature [4]. Development of highly selective unsupported catalysts for lignin depolymerization would contribute to the first step of biomass conversion.

Activation of C—O bonds has become the focus of interest for catalytic lignin degradation and conversion, due to its importance for the conversion of oxygen-rich biomass to deoxygenated fuels and commercial chemicals. Aliphatic C—O bonds in cellulose and lignin can be cleaved with hydrolysis and dehydration [6]. On the other hand, breaking C—OAr (Ar = aromatic ring) and O—Ar bonds is challenging because of the strength and stability of these linkages [7]. Of all the C—O bond containing linkages, β—O—4 is the most abundant linkage type in lignin [8,9], which can be denoted as Ar—C—C—O—Ar. The fragmentation of the C—OAr linkage tends to generate water-soluble compounds containing phenolic hydroxyl groups [8]. Investigations have been carried out on C—O activation of lignin model compounds in solutions [10–14]. Ekerdt and coworkers have studied β—O—4 cleavage in ionic liquids/metal solutions [10–12]. In a recent study, they discovered that in a solution of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and water, FeCl₃, CuCl₂, and AlCl₃ effectively cleave the β—O—4 bond of guaiacylglycerol-β-guaiacyl ether at 150 °C [12]. In addition to C—O bond cleavage, a process of β—O—4 linkage activation often involves hydrogenation or hydrogen transfer. Effective transition metals catalysts have been used for β—O—4 cleavage. For instance, Nichols et al. developed a ruthenium-catalyzed C—O bond

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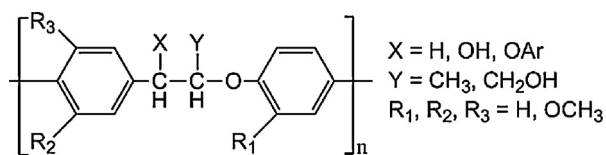
Fig. 1. β—O—4 linkage of lignin.

cleavage of 2-aryloxy-1-arylethanols (Ar—CH(OH)—CH$_2$—O—Ar', Fig. 1) and poly(4'-hydroxy-1-phenethanol) at 175 °C [13]. In their experiments, a sets of phosphine ligands are considered, including monodentate, bidentate and tridentate ligands, in which the wide-bite angle ligand, 9,9-dimethyl-bis(diphenylphosphino)-xanthene (Ph-xantphos) provided a 99% yield in breaking Ar—CH(OH)—CH$_2$—O—Ar' into Ar—COCH$_3$ and Ar'—OH [12]. The proposed reaction mechanism involves C—O bond cleavage and hydrogenation reaction [13]. Although above studies suggest promising potentials of those transition metal catalysts in biomass conversion, the catalytic properties of the metal centers and the specific role of the ligands/solvents were not explored. Thus, studying the reaction thermodynamics with regards to metal and ligand effects would help better understand the catalytic mechanism and the properties of the transition metal catalysts.

The Ph-xantphos ligand (its coordination type is denoted as "POP"), which was utilized in experiments by Nichols et al., belongs to a family of ligands known as pincer ligands [15]. More popular coordination types of these ligands include PNP, NNN, PCP, NCN, etc [16–25]. A common structure of these ligands is demonstrated in Fig. 2. Pincer complexes have raised great attention in homogeneous catalysis due to their efficient catalytic properties, extraordinary thermal stability, given their high melting points [26–29]. For instance, the complex (PCP)Ir (PCP = κ3-C$_6$H$_3$-2,6-[CH$_2$P(t-Bu)$_2$]$_2$) and its derivatives are known as the most effective alkane dehydrogenation catalysts developed to date [30–32]. In addition, studies have shown that pincer complexes are catalytically active in activation of C—E bonds (E≡C, O, F, N, etc.) [15]. For C—O bond activation, specifically, Choi et al. recently reported that (PCP)Ir (PCP = κ3-C$_6$H$_3$-2,6-[CH$_2$P(t-Bu)$_2$]$_2$) undergoes oxidation addition of C(sp^3)—O bonds of ethers, esters and tosylates, via initial activation of a C—H bond. Yang et al. [33] also discovered a cationic Ir PCP complex that catalytically cleaves an ether C—O bond in the presence of HSiEt$_3$. The catalysis results in R—H and ROSiEt$_3$. On the other hand, some pincer complexes have been shown to have the ability to catalyze hydrogen transfer and hydrogenation reactions [34,35]. Gunanathan et al. have studied the H$_2$ activation and hydride transfer using a PNP type Ru carbonyl complex via both experimental and computational approaches. Their results showed that the Ru center splits H$_2$ into a proton and a hydride group heterolytically. Zhang et al. investigated the PNP and PNN type Ru hydrido borohydride complexes for the hydrogenation of esters [22]. Studies showed that under relative low temperature and pressure (110 °C and 10 atm), these complexes (especially the PNN complex) were able to catalyze the hydrogenation of nonactivated esters to the corresponding alcohols under mild pressure of H$_2$, in neutral and homogeneous conditions.
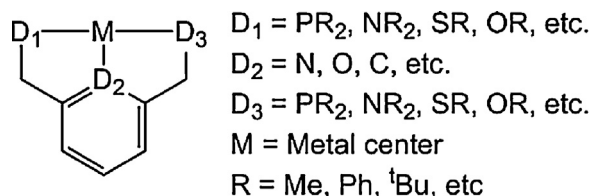
In addition to the ligand, the metal center plays an important role in C—O activation and hydrogenation. Our previous computational studies have been focused on intrinsic catalytic properties of transition metals in catalyzing CO$_2$ activation and hydrogenation [36–39], as well as C—O bond activation of dimethyl ether [40]. In the studies of the reverse water-gas shift reactions mediated by 3d metal β-diketiminate complexes, we discovered that earlier 3d species tend to have stronger binding interactions with CO$_2$ and more exergonic C—O cleavage reactions than later metal systems, while the opposite energetic trend as a function of metal was obtained for the hydrogenation of the oxo complex intermediate [36,38]. These trends suggested that middle series metal complexes (Mn, Fe and Co) gave the lowest fluctuations on reaction energetics along the pathway, and therefore, are thermodynamically more favorable. The trend of binding CO$_2$ and activating the C—O bond was also observed in our study of CO$_2$ reduction to CO on middle to late 3d metal (Fe, Co, Ni and Cu) surfaces [37,38]. Recently, we studied transition metal ion mediated C—O bond cleavage of dimethyl ether (DME) in gas phase using density functional theory (DFT) and CCSD(T) methods [40]. Late 3d metals Fe, Co, Ni and Cu, and 4d metals Ru, Rh, Pd and Ag were considered with +1 charge. The reaction thermodynamics indicated that for both 3d and 4d systems, earlier metals tend to have more exergonic reactions and lower barriers in breaking the C—O bond. Fe and Ru showed the most favorable thermodynamics of all the metals considered [40]. These energetic trends for CO$_2$ and DME activation determined the intrinsic catalytic properties of metals for C—O activation.

Based on our previous research [36–40] and inspired by the report of Nichols et al., [13] in this paper we report a DFT study on the reaction mechanisms of C—O bond cleavage of Ar—CH(OH)—CH$_2$—O—Ar' (Fig. 1) using group 8 (Fe, Ru and Os) pincer complexes. Group 8 metals have been widely utilized in pincer complexes [41], in which, with neutral ligands such as PNP and NNN, the metal center has an oxidation state of either (0) or (II), while with monoanionic ligands like PCP and NCN, the metal center will mostly have an oxidation state of (IIc) [41]. These monoanionic ligands contain an aryl anion, which is connected to the metal atom through a σ bond. Table 1 shows the combinations of metal oxidation states that were considered in this study. The β—O—4 model compound considered in this study is the monomer structure shown in Fig. 1, 2-phenoxy-1-phenethanol, where X=OH, Y=H and R$_1$ = R2 = R3 = H.

Since we are going to exclusively explore the catalytic properties of metal centers and the pincer ligands, the metal complexes considered in this study only contain a pincer ligand and a metal center, excluding other common ligands in pincer complexes, such as N$_2$ and Cl. It is assumed that these small ligands do not play a significant role in the catalysis of C—O bond cleavage. The proposed reaction mechanisms are shown in Fig. 3. Two possible reaction pathways can lead to complex 8, in which route B is similar with the mechanism proposed by Nichols et al. [13] Route A starts with an oxidative addition reaction where the catalyst binds the beta oxygen of 1 to form an adduct 2. Then the β—C—O bond of this adduct is broken through the metal center and forms compound 3, in which the β-carbon and the oxygen are both bound to the metal. In this step, the C—OPh bond is cleaved instead of the CO—Ph bond

D$_1$ = PR$_2$, NR$_2$, SR, OR, etc.
D$_2$ = N, O, C, etc.
D$_3$ = PR$_2$, NR$_2$, SR, OR, etc.
M = Metal center
R = Me, Ph, ^{t}Bu, etc

Fig. 2. Typical structures of pincer complexes.

Table 1
Considered ligands and oxidation states of metal center.

Ligand	D$_1$	D$_2$	D$_3$	Oxidation state of metal center
PNP	PH$_2$	N	PH$_2$	0
NNN	NH$_2$	N	NH$_2$	0
PCP	PH$_2$	C	PH$_2$	II
PCN	PH$_2$	C	NH$_2$	II
NCN	NH$_2$	C	NH$_2$	II