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Effective C–O Bond Cleavage of Lignin β-O-4 Model Compounds: A New $RuHCl(CO)(PPh_3)_3$/KOH Catalytic System

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Abstract Base, especially KOH, can be used in place of xantphos for the Ruthenium-complex-catalyzed C–O bond cleavage of β-O-4 lignin model compounds. In the presence of KOH, $RuHCl(CO)(PPh_3)_3$ and $Ru(H)_2(CO)(PPh_3)_3$ show the best catalytic effect among several ruthenium-complexes studied.

Keywords Lignin · Homogeneous catalysis · KOH · β-O-4 cleavage

1 Introduction

At the present time, lignocellulosic biomass is valued as a source for the production of renewable chemicals and fuels in light of diminishing fossil fuel reserves and increasing demand for energy [1, 2]. Lignin is a complicated three dimensional polymer linked by ether bonds and C–C bonds such as α-O-4, β-O-4, β-1, β-5 and 5–5 types [3], among which β-O-4 linkage comprises some 50–60 % of the lignin structures [4]. Lignin comprises a large mass proportion (15–30 % by weight) and energy content (up to 40 %) of the lignocellulose [5], and it is recalcitrant to chemical and biological conversion [6]. As a result, a large effort is underway to develop mild, less-energy-intensive and eco-friendly methods to convert lignin into small molecules that can be upgraded into a fuel stream or chemicals [7].

Studies on degradation of lignin and lignin models include bacterial degradation [8], heterogeneous Co(salen)-catalyzed oxidation using H_2O_2 under microwave radiation [9], hydrolytic cleavage in an ionic liquid in the presence of $FeCl_3$, $CuCl_2$, or $AlCl_3$[10] depolymerization in alcohol over nickel-based catalysts [11], and vanadium-catalyzed nonoxidative degradation [12, 13].

In 2010 Nichols et al. [14] reported a $Ru(H)_2(CO)(PPh_3)_3$/xantphos catalyst that is capable of effectively degrading β-O-4 models as well as a synthetic β-O-4 linked polymer under N_2 as shown below (Fig. 1). The catalytic system was studied in detail by Wu et al. [4], and a plausible mechanism was proposed. This research is meaningful because of the large mass proportion of β-O-4 linkage in lignin structure. It is also the first reported ruthenium-catalyzed dehydrogenation and then hydrogenation to create mixtures of monofunctional carbonyl and phenolic products. However, the studies conclude that addition of a wide bite angle phosphine ligand [15], namely xantphos, to the $Ru(H)_2(CO)(PPh3)_3$ system is necessary for efficient reactivity, which leads to inapplicability of the catalytic system for practical uses because of the high price.

In this study, we report that $RuHCl(CO)(PPh_3)_3$ and $Ru(H)_2(CO)(PPh_3)_3$ in the presence of some bases such as KOH, can perform well without the addition of xantphos. The major advantage of using an inorganic base such as

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KOH lies in its low cost relative to the organic ligand and its ability to be recycled because of its insolubility in the organic reaction media.

2 Results and Discussions

Table 1 summarizes the results of a series of reaction of 2-(2-methoxyphenoxy)-1-phenylethanol (**2**) under various conditions. In the absence of KOH (entry **3**), no products were observed, which is consistent with earlier studies [4, 14]. However, addition of KOH to the $RuHCl(CO)(PPh_3)_3$ system greatly increases catalytic activity (entry **2**), proving the role of base in the catalytic degradation of **2**. The same treatment to $Ru(H)_2(CO)(PPh_3)_3$ system is also proved to be effective(entry **4**). When KOH is used in the absence of a ruthenium catalyst (entry **1**), consumption and yields of products were shown but at a relative low level. A small amount of 1-phenylethyl alcohol was detected. The formation of acetophenone (A) and guaiacol (B) can be explained by the well-known base catalyzed hydrolysis of β-O-4 structure as shown in Fig. 2 [16, 17]. The formation of 1-phenylethyl alcohol (C) is hard to rationalize as it involves reductive cleavage. This needs to be clarified by further studies. Nevertheless, it is clear that KOH can be used in place of xantphos in the catalytic degradation of **2**.

Whether KOH could transform $RuHCl(CO)(PPh_3)_3$ to another Ru-complex and eventually contribute to the degradation of **2** is another important question. In the $RuCl_2(PPh_3)_3$-catalyzed transfer-hydrogenation of ketones, addition of a catalytic amount of base dramatically accelerates the rate [18, 19]. The experimental results indicate that the role of the base is to transform the unreactive $RuCl_2(PPh_3)_3$ into the catalytically active $Ru(H)_2(PPh_3)_3$ (Fig. 3). However, in the present study, $RuHCl(CO)(PPh_3)_3$ is as effective, if not more, as $Ru(H)_2(CO)(PPh_3)_3$ (entry **2** and entry **4**, Table 1). Therefore, KOH may play

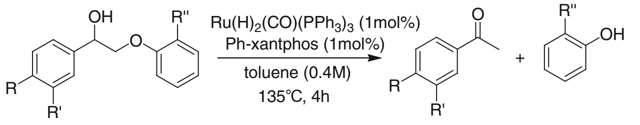


Fig. 1 The reaction studied by Nichols et al. [14], $Ru(H)_2(CO)(PPh_3)_3$/xantphos catalyst under N_2

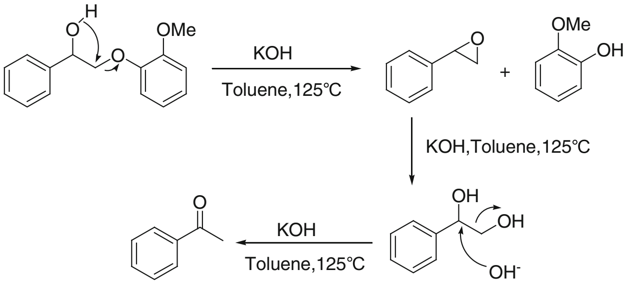
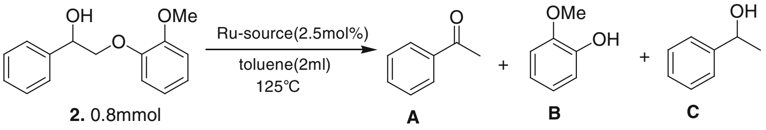


Fig. 2 Alkali catalyzed hydrolysis reaction of 2-(2-methoxyphenoxy)-1-phenylethanol

Table 1 C–O bond cleavage of 2-(2-methoxyphenoxy)-1-phenylethanol catalyzed by $RuHCl(CO)(PPh_3)_3$ with and without KOH



Entry[a]	Ru-source (2.5 mol%)	KOH (50 mol%)	Cons. (%)[b]	Yield %[b]			Time (h)
				A	B	C	
1	None	Y	60	12	6	10	12
			57	15	9	15	24
			62	13	11	15	36
			70	15	7	16	48
2	$RuHCl(CO)(PPh_3)_3$	Y	50	38	15	0	12
			74	62	39	0	24
			93	80	75	0	36
			95	71	65	0	48
3	$RuHCl(CO)(PPh_3)_3$	N	0	0	0	0	36
4	$Ru(H)_2(CO)(PPh_3)_3$	Y	97	63	16	0	48

[a] Reactions were run in a Schlenk flask under an atmosphere of purified argon equipped with condenser

[b] Yields and consumptions were determined by GC relative to an internal standard

other roles in addition to the transformation of RuHCl(CO)$(PPh_3)_3$ into $Ru(H)_2(CO)(PPh_3)_3$. We will show that KOH is also effective in other related ruthenium catalytic systems (*vide infra*).

We also investigated the effectiveness of several other bases on the degradation of **2** with $RuHCl(CO)(PPh_3)_3$ including NaOH, KO^tBu, K_2CO_3, and NEt_3, among which KOH is the best one followed by KO^tBu and NaOH, K_2CO_3 and NEt_3 are the least functioning bases. The results suggest basicity, steric factors and compatibility with the solvent may all contribute to their effectiveness.

The substrates in Table 2 model the substitution patterns found in lignin. Increasing the substitution on Ar' has a negative influence on both consumption and yield, while methoxylation of Ar has relatively little effect on the reaction. These results (entries **1**–**5**) are in agreement with those of Nichols et al. [14]. As for substrate 6, we found notable yield decrease of Ar'OH and absence of $ArCOCH_3$, at the same time, a new product was detected. GC–MS analysis identified its structure as 2-Methoxy-4-vinyl-phenol, indicating that the OH on Ar could not only influence the yield but also the mechanism of the reaction. It is conceivable that ArOH may coordinate with ruthenium center, generating an inactive complex.

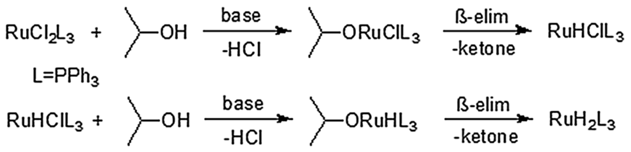


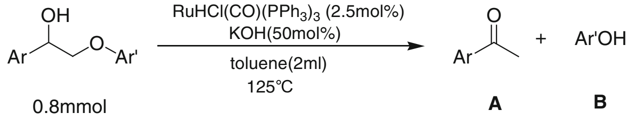
Fig. 3 The role of base in the $RuCl_2(PPh_3)_3$-catalyzed transfer-hydrogenation of ketones

Wu and coworkers showed that in the hydrogenolysis of 2-(2-methoxyphenoxy)-1-phenyl-1,3-propanediol with a $Ru(H)_2(CO)(PPh_3)_3$/xantphos catalyst [4], three products were formed, guaiacol, 3-hydroxy-2-(2-methoxyphenoxy)-1-phenyl-1-propanone and 2-(2-methoxyphenoxy)-1-phenyl-ethanone. Guaiacol was formed in less than 15 % yield and without the concurrent formation of acetophenone. The authors convincingly showed that guaiacol was formed with concurrent formation of an inactive ruthenium catalyst complex. While 2-(2-methoxyphenoxy)-1-phenyl-ethanone is apparently formed via reverse aldol reaction from 3-hydroxy-2-(2-methoxyphenoxy)-1-phenyl-1-propanone [4], the formation of the latter clearly indicates that the catalytic system is capable of dehydrogenating the benzyl alcohol to the corresponding ketone. The latter is also capable of forming an inactive complex with the catalytic system [4], therefore limiting the yield of guaiacol.

We also applied this catalytic system to hydrogenolysis of 2-(2-methoxyphenoxy)-1-(3,4-dimethoxy)phenyl-1,3-propanediol (**7**), The result showed 4 staple products, all having relatively low yields (Table 3). Nevertheless, the consumption and yield of guaiacol are higher than those reported by Nichols et al. [4]. In our catalytic system with KOH, both α- and γ-OH of the starting compound can produce guaiacol (B) via epoxide formation [16, 17], giving an extra amount of guaiacol. The rearrangement of epoxide followed by reverse aldol reaction then gives either acetoveratrone (A) or veratryl aldehyde (C). The starting compound will also produce guaiacol via complexation with the catalyst, resulting in an inactive catalyst [4].

In order to test the influence of KOH on the catalytic effect of other ruthenium-complex, we investigated

Table 2 C–O bond cleavage of various 2-aryloxy-1-arylethanols



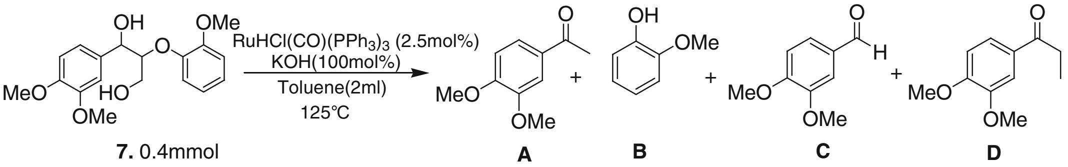
Substrate[a]	Ar	Ar'	Cons. (%)[b]	Yield %[b]		Time (h)
				A	B	
1	C_6H_5	C_6H_5	99	86	84	12
2	C_6H_5	2-(CH_3O)-C_6H_4	93	80	75	36
3	C_6H_5	2,6-$(CH_3O)_2$-C_6H_3	41	30	4	24
4	4-(CH_3O)-C_6H_4	C_6H_5	91	80	77	12
5	3,4-$(CH_3O)_2$-C_6H_3	2-(CH_3O)-C_6H_4	95	66	45	24
6	3-(OH)-4-$(CH_3O)_2$-C_6H_3	2-(CH_3O)-C_6H_4	89	ND[c]	14	24

[a] Reactions were run in a Schlenk flask under an atmosphere of purified argon equipped with condenser

[b] Yields and consumptions were determined by GC relative to an internal standard

[c] Not detected

Table 3 C–O bond cleavage of 2-(2-methoxyphenoxy)-1-(3,4-dimethoxy)phenyl-1,3-propanediol



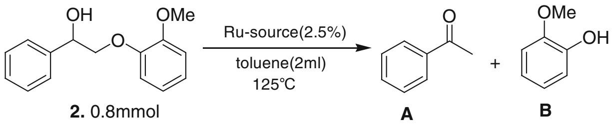
Ru-source (2.5 mol %)	Cons. (%)[b]	Yield %[b]				Time (h)
		A	B	C	D	
$RuHCl(CO)(PPh_3)_3^a$	95	4	18	5	N[c]	12
	94	6	26	7	N[c]	24
	89	6	26	8	N[c]	36
	91	4	53	11	N[c]	48

[a] Reactions were run in a Schlenk flask under an atmosphere of purified argon equipped with condenser

[b] Yields and consumptions were determined by GC relative to an internal standard

[c] Minor and not quantitated

Table 4 C–O Bond Cleavage of 2-(2-methoxyphenoxy)-1-phenylethanol catalyzed by other Ru-complex with and without KOH



Entry[a]	Ru-source (2.5 mol %)	KOH (50 mol %)	Cons. (%)[b]	Yield %[b]		Time (h)
				A	B	
1	$RuH_2(CO)(PPh_3)_3$	Y	97	63	16	48
		N	30	12	13	48
2	$RuCl_2(PPh_3)_3$	Y	79	57	34	48
		N	26	0	0	48
3	$RuCl_2(COD)$	Y	82	62	24	48
		N	10	0	0	48
4	$Ru(methallyl)_2(COD)$	Y	79	56	26	48
		N	10	2	2	48
5	$RuClCp(PPh_3)_3$	Y	54	24	16	48
		N	8	0	0	48
6	$RuH_2(PPh_3)_4$	Y	56	22	11	48
		N	21	0	3	48
7	$Ru_3(CO_{12})$	Y	56	34	24	48
		N	0	0	0	48

[a] Reactions were run in a Schlenk flask under an atmosphere of purified argon equipped with condenser

[b] Yields and consumptions were determined by GC relative to an internal standard

catalytic cleavage of **2** by other ruthenium-complexes. The results are shown in Table 4. While the effectiveness of different catalytic system varies to a great extent, it is clear that KOH could dramatically increase the catalytic effect of all ruthenium-complexes. Without KOH, none of the catalytic system is effective. No better results were obtained in comparison with $RuHCl(CO)(PPh_3)_3$. It seems that the ease of selective substitution of phosphine ligand *trans* to H^- in *cis*,*mer*-[$RuHCl(CO)(PPh_3)_3$] by alkoxy from **2** provide clear evidence for the kinetic *trans* effect of the

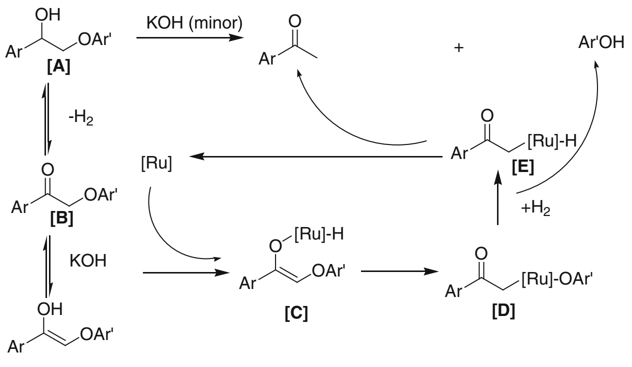


Fig. 4 Plausible mechanism for C–O bond cleavage

strong σ-donor hydrido ligand [20]. The carbon monoxide, which acts as a weak σ-donor but a strong π-acceptor ligand, is ideal for tuning the electronic and steric properties of the Ru center in the reaction intermediates [21]. The presence of ligands, which increases the electron density on the Ru, reduces the catalytic activity.

Based on prior research by Nichols and co-workers [14] and Wu and co-workers[4] along with our results, we proposed a mechanism (Fig. 4). The steps include the dehydrogenation of 2-aryloxy-1-arylethanol [A] according to those postulated in previous studies on Ru-catalyzed dehydrogenation. The equilibrium between keto form and enol form of aryloxy-1-arylethanone [B] are accomplished with the assistance of KOH, which combined with [Ru] in the formation of ruthenium enolate [C]. C–O activation in [C] leads to ruthenium complex [D]. Hydrogenation of [D] yields a Ru-monohydride enolate [E] and releases phenol Ar'OH followed by reductive elimination of the ketone ArC(=O)CH_3 and association with [B] to close the cycle. In addition to facilitate keto enol tautomerism, KOH might also involve in the ruthenium complex system. This is a subject requiring further investigation.

In conclusion, we found that base, especially KOH, can be used in place of xantphos in catalytic cleavage of C–O bond of 2-aryloxy-1-arylethanols using several ruthenium based complexes. Among them, $RuHCl(CO)(PPh_3)_3$ and $Ru(H)_2(CO)(PPh_3)_3$ show the best catalytic effect.

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