

Catalytic behavior of a Wool–Pd complex in asymmetric hydrogenation of diacetone alcohol and 3-methyl-2-butanone

Mao-Ya Yin, Guo-Li Yuan^{*}, Mei-Yu Huang, Ying-Yan Jiang

Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, Beijing 100080, China

Abstract

A Wool–Pd complex has been found to be able to catalyze the asymmetric hydrogenation of diacetone alcohol to (*R*)-2-methyl-2,4-pentanediol and 3-methyl-2-butanone to (*R*)-3-methyl-2-butanol at 30°C and under 1 atm H₂. The optical yields were greatly affected by Pd content in Wool–Pd complex. When a proper Pd content was selected, (*R*)-2-methyl-2,4-pentanediol and (*R*)-3-methyl-2-butanol could be obtained in 73 and 100% optical yield, respectively. This chiral natural biopolymer–Pd complex catalyst was easy to prepare and could be reused without appreciable change in optical catalytic activity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Wool–Pd complex; Diacetone alcohol; Asymmetric hydrogenation

1. Introduction

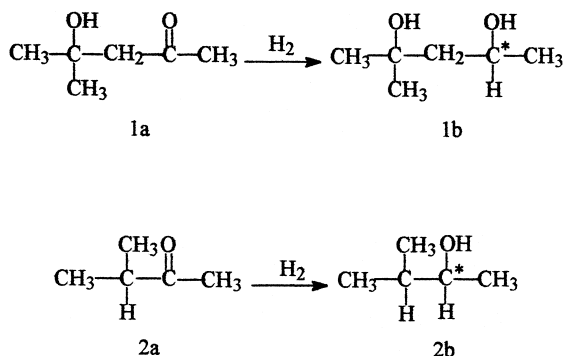
A silk–Pd complex [1] has been found early to be able to catalyze the asymmetric hydrogenation of some unsaturated compounds, especially imines, but the optical yields were not so high. In a previous paper [2], a palladium complex of Wool (abbreviated as Wool–Pd) has been found to catalyze the hydrogenation of nitrobenzene, benzaldehyde, allyl alcohol, vinylacetate, styrene and hexene-1 to aniline, benzyl alcohol, 1-propanol, ethyl acetate, ethyl benzene and hexane respectively in high yield under mild conditions. However, Wool–Pd complex catalyst has not been used in the asymmetric hydrogenation. Silk and Wool are chiral

natural biopolymers, but both structures are fairly different. Wool is a natural polymer of amino acids crosslinked by S–S bonds. Silk is also a natural polymer of amino acids, but it does not contain S–S bond crosslinking unit in the structure. The main component of Wool is keratin, and it is insoluble in any solvent, so the optical rotation cannot be determined. When the S–S bonds in keratin are broken by reducing agent to –SH groups, the keratin aqueous solution can be obtained, and the optical rotation, $[\alpha]_D^{25}$ is -55° [3]. Naturally, the insoluble keratin, Wool, can be used as chiral polymer ligand directly. The N and S atoms in Wool may coordinate to transition metal ion to form chiral Wool–metal complex.

Recently, the Wool–Pd complex has been found to be able to catalyze the asymmetric hydrogenation of diacetone alcohol (**1a**) to (*R*)-2-methyl-2,4-pentanediol (**1b**), and 3-methyl-2-

^{*} Corresponding author. Tel.: +86-10-6255-9368; Fax: +86-10-6255-9368.

butanone (**2a**) to (*R*)-3-methyl-2-butanol (**2b**) respectively at 30°C and under 1 atm H₂.



The optical yields of these chiral alcohols are greatly affected by the Pd content in Wool–Pd complex catalyst. This chiral natural biopolymer–Pd complex catalyst was very easy to prepare and could be reused without appreciable change in optical catalytic activity.

2. Experimental

2.1. Preparation of Wool–Pd complex

Common commercial white Wool was washed with water and ethanol, then cut with scissors to very short pieces.

Several samples of Wool–Pd complex with different Pd content were prepared by the reaction of a definite amount of Wool pieces with PdCl₂ · 2H₂O in ethanol solution.

For example, in order to obtain a sample of 0.30 mmol/g of Pd content in Wool–Pd complex, 0.1 g of Wool pieces, 0.03 mmol PdCl₂ · 2H₂O (in small amount ethanol) and 5 ml of ethanol were placed in a 25 ml flask equipped with magnetic stirrer and a reflux condenser. The mixture was stirred and refluxed for about 3 h to cause white wool pieces to become dark grey, and the solution to become colorless and transparent from brown. The product was filtered, washed with ethanol and dried to obtain about 0.1 g of dark grey pieces (Wool–Pd).

2.2. Hydrogenation of ketones

0.1 g of catalyst (Wool–Pd), 0.1 g of ketone and 5 ml of solvent (ethanol) were placed in 25 ml flask equipped with magnetic stirrer and a hydrogen inlet tube which was connected to a hydrogen volume measuring burette and a hydrogen storage cylinder. The hydrogenation reaction system was alternatively evacuated and flushed with hydrogen for several times, and the hydrogenation was carried out at 30°C and under 1 atm H₂ for 10 h. Then the reaction mixture was filtered in order to separate and recover the catalyst. Sometimes, the recovered catalyst was reused. The composition of the hydrogenation products was analyzed by GC and the optical rotation was measured by polarimeter.

3. Results and discussion

Table 1 shows the X-ray photoelectron spectroscopy (XPS) data for Wool–Pd, Wool and PdCl₂. It can be seen that there are two oxidation states of Pd, Pd(0) and Pd(II), in Wool–Pd

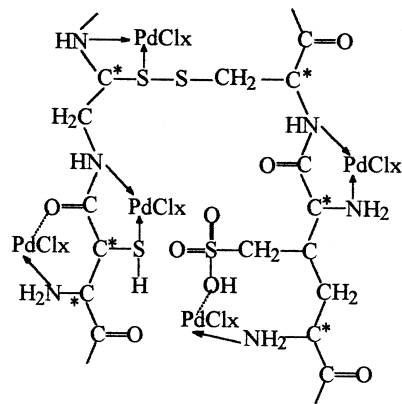
Table 1
X-ray photoelectron spectroscopy (XPS) data for Wool–Pd, Wool and PdCl₂

Sample	Element and state	Binding energy (eV)	Content (%)
PdCl ₂	Pd(II) _{3d 5/2}	337.8	
Wool–Pd	Pd(0) _{3d 5/2}	336.1	74.9
	Pd(II) _{3d 5/2}	337.7	25.1
Wool	N _{1s} –NH–CO–	400.0	21.6
	–NH ₂	398.8	78.4
Wool–Pd	N _{1s} –NH–CO–	400.4	14.8
	–NH ₂	399.4	85.2
Wool	S _{2p} –SO ₃ H	167.8	13.2
	–SH	163.6	50.2
	–S–S–	164.8	37.6
Wool–Pd	S _{2p} –SO ₃ H	167.6	13.7
	–SH	162.7	13.3
	–S–S–	164.0	73.0
Wool	O _{1s}	531.7	
Wool–Pd	O _{1s}	531.9	

complex. Probably, a part of PdCl_2 was converted to $\text{Pd}(0)$ during the preparation of Wool–Pd complex. There are two kinds of nitrogen containing group, $-\text{NH}-\text{CO}-$ and NH_2 , in Wool, and N_{1s} binding energy and the content for them are different. Such data in Wool–Pd are also different from those in Wool. The difference of N_{1s} binding energy between $-\text{NH}-\text{CO}-$ in Wool and $-\text{NH}-\text{CO}-$ in Wool–Pd is 0.4 eV, and that between $-\text{NH}_2$ in Wool and $-\text{NH}_2$ in Wool–Pd is 0.6 eV. There are three kinds of S containing group, $-\text{SO}_3\text{H}$, $-\text{SH}$ and $-\text{S}-\text{S}-$, in Wool, and the content and S_{2p} binding energy for them are different. Such data in Wool–Pd are also different from those in Wool. The difference of S_{2p} binding energy between $-\text{SO}_3\text{H}$ in Wool and $-\text{SO}_3\text{H}$ in Wool–Pd is only 0.2 eV, that between $-\text{SH}$ in Wool and $-\text{SH}$ in Wool–Pd is 0.9 eV, and that between $-\text{S}-\text{S}-$ in Wool and $-\text{S}-\text{S}-$ in Wool–Pd is 0.8 eV. The difference of O_{1s} binding energy between Wool and Wool–Pd is only 0.2 eV.

These results show that coordination or ionic bonds are formed by the connection of N atoms (in $-\text{NH}-\text{CO}-$ and $-\text{NH}_2$) and S atoms (in $-\text{SH}$ and $-\text{S}-\text{S}-$) with Pd atoms in the Wool–Pd

complex. And only a little amount of O atoms are concerned to form the complex. The structure of Wool–Pd may be shown as follows:



Wool-Pd

Table 2 shows the results of the asymmetric hydrogenation of diacetone alcohol and 3-methyl-2-butanone catalyzed by Wool–Pd complex. The yields of alcohol were all obtained in about 100%, so we did not show them in the table. It can be seen from the table that the optical yields are greatly affected by the Pd

Table 2

Asymmetric hydrogenation of diacetone alcohol and 3-methyl-2-butanone catalyzed by Wool–Pd complex

Ketone	Pd content in Wool–Pd (mmol/g)	Number of used times of catalyst	Alcohol	
			Optical yield ^a (%)	Absolute configuration ^b
Diacetone alcohol	0.12	1	44.9	R
	0.18	1	45.4	R
	0.24	1	60.1	R
	0.30	1	72.7	R
	0.30	2	73.3	R
	0.48	1	33.7	R
3-methyl-2-butanone	0.12	1	54.4	R
	0.18	1	79.7	R
	0.24	1	100	R
	0.24	2	99.5	R
	0.30	1	100	R
	0.30	2	100	R
	0.48	1	87.5	R

Catalyst, Wool–Pd, 0.1 g; Ketone, 0.1 g; Solvent, 5 ml ethanol; 30°C, 1 atm H_2 , 10 h.

^aOptical yields were calculated on the basis of reported values for the specific rotation of pure enantiomer: (*R*)-2-methyl-2,4-pentanediol, $[\alpha]_D^{25} + 15.0^\circ$ (c 1, EtOH) 92% ee [4]; (*R*)-3-methyl-2-butanol, $[\alpha]_D + 5.3^\circ$ (neat) [5].

^bDetermined by the sign of optical rotation.

content in Wool–Pd complex in both cases. And in the case of hydrogenation of diacetone alcohol (**1a**) to (*R*)-2-methyl-2,4-pentanediol (**1b**), the optical yield amounts to 72.7% at 0.3 mmol Pd/g in Wool–Pd complex. When the catalyst is reused, the optical yield is changed to 73.3%. It shows that the optical catalytic activity is almost not changed, so the catalyst is very stable for reusing.

It has been reported that (*R*)-2-methyl-2,4-pentanediol (**1b**) could be obtained by resolution of racemic mixture via lipase catalysis in organic solvent [4]. Obviously, such a method is not convenient and not economical.

In the case of asymmetric hydrogenation of 3-methyl-2-butanone (**2a**) to (*R*)-3-methyl-2-butanol (**2b**), 100% optical yield was obtained at 0.24 and 0.30 mmol Pd/g, and the optical yield is changed to 99.5 and 100% when the Wool–Pd complex catalyst was reused. In this case, the catalyst is also demonstrated to be very stable in reusing.

It has been reported that **2a** to **2b** could be carried out by asymmetric reduction with a reagent prepared from (*S*)-2-amino-3-methyl-1,1-diphenylbutan-1-ol and borane [5]. However, such a reduction method using reagent is not economical. **2b** could also be obtained by asymmetric transfer hydrogenation of methyl iso-propyl ketone using phosphine–rhodium

complex catalyst [6]. However, the optical yield is very low, < 5%.

As shown above, the structure of Wool–Pd complex catalyst is very complicate. From such a structure and the data of XPS, it is not difficult to imagine that the catalytic behaviors of Wool–Pd are easily changed by changing Pd content in the complex. Such an imagination was supported by the experimental results.

Wool is a very abundant and cheap chiral natural biopolymer ligand. And Wool–Pd complex catalyst was very easy to prepare in several hours, and could be reused without appreciable change in optical catalytic activity.

Only two examples were illustrated in above experiments, but probably, many other prochiral compounds can be used to show interesting results by Wool–Pd complex catalyst.

References

- [1] S. Akabori, Y. Izumi, Y. Fujii, S. Sakurai, *Nature* 178 (1956) 323.
- [2] X.P. Song, M.Y. Huang, Y.Y. Jiang, *J. Mol. Catal. (China)* 8 (1994) 8.
- [3] K. Yamauchi, *Polymer Application (Japan)* 43 (1994) 14.
- [4] G. Kircher, M.P. Scollar, A.M. Klibanov, *J. Am. Chem. Soc.* 107 (1985) 7072.
- [5] S. Itsuno, K. Ito, A. Hirao, S. Nakahama, *J. Org. Chem.* 49 (1984) 555.
- [6] R. Spogliarich, J. Kaspar, M. Graziani, *J. Organomet. Chem.* 306 (1986) 407.