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Mendeleev Commun., 2010, **20**, 218–219
Mendeleev Communications

Selective photoinduced oxidation of 2,3,5-trimethylphenol to 2,3,5-trimethylbenzoquinone catalyzed by hypocrellins/$CuCo_2O_4$

Ying Li,* Wei Liu, Mingzhu Wu, Zhongzhou Yi and Jucheng Zhang

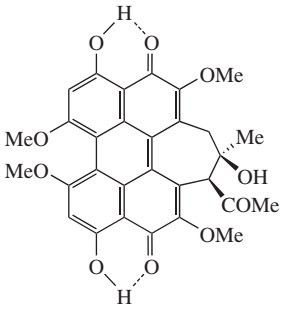
Key Laboratory of Natural Pharmaceutical & Chemical Biology of Yunnan Province, Honghe University, Mengzi, 661100, P. R. China. Fax: +86 873 369 9092; e-mail: yingli921@gmail.com

DOI: 10.1016/j.mencom.2010.06.012

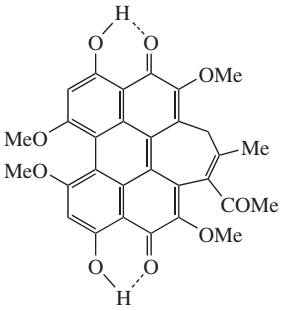
The title reaction afforded 2,3,5-trimethylbenzoquinone with a high selectivity (nearly 100%) at a 7.3% conversion of 2,3,5-trimethylphenol under irradiation with visible light (> 400 nm) in an aerobic atmosphere.

Photocatalytic processes in a homogeneous phase or heterogeneous system are of importance.[1] Photocatalysts were used to decompose organic pollutants[2,3] and to produce hydrogen.[4,5] The selective oxidation of hydrocarbons or alcohols by molecular oxygen under irradiation with visible light can be performed using photocatalysts such as TiO_2,[6] zeolite,[7] ruthenium complexes,[8] Cr–SiO_2,[9] $MgBr_2{\cdot}Et_2O$[10,11] and heteropolyoxometalate.[12] However, the photooxidation of phenols to benzoquinones using heterogeneous photocatalysts is poorly understood.[13]

2,3,5-Trimethylbenzoquinone (TMQ), an important intermediate of vitamin E, results from the oxidation of 2,3,5-trimethylphenol (TMP) or 2,3,6-trimethylphenol.[14–17] We found that $CuCo_2O_4$ showed an outstanding catalytic activity and selectivity in the oxidation of TMP to TMQ with an excess of 30% aqueous hydrogen peroxide.[18]

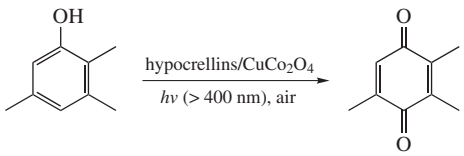


Hypocrellin A



Hypocrellin B

Hypocrellins, including hypocrellin A and hypocrellin B, are photosensitizers naturally occurring in the fungus *Hypocrella bambusae* from the Yunnan province, China.[19,20] Hypocrellins can be used for catalytic oxidation in organic syntheses.[13] Here, we report the highly selective photooxidation of TMP to TMQ using hypocrellins/$CuCo_2O_4$ (HC/CCO) as a catalyst prepared by physical adsorption under mild conditions.†



TMP TMQ

To test the efficiency of different HC/CCO catalysts, their catalytic activity was examined in the photooxidation of TMP under visible light (> 400 nm) in ethanol at room temperature.

Table 1 Effect of HC/CCO ratio.[a]

Entry	Catalyst, hypocrellins:$CuCo_2O_4$ ratio	Conversion of TMP (mol%)
1	Hypocrellins	0.15
2	5:100	2.7
3	8:100	5.1
4	10:100	7.3
5	10:100 (without air)	1.4
6	10:100 (recycled)	7.4
7	12:100	7.5
8	12:100 (recycled)	7.2
9	15:100	7.8
10	15:100 (recycled)	7.3
11	$CuCo_2O_4$	0.0
12	No catalyst	0.0
13	10:100 (without irradiation)	0.0

[a]Reaction conditions: 1 mmol of TMP; 100 mg of catalyst; solvent, 50 ml of ethanol; reaction time, 12 h; reaction temperature, 25±3 °C; irradiation, > 400 nm visible light; oxidation, air (10 ml min^{-1}). In all experiments the selectivity of TMQ was 100%.

The conversion of TMP and the selectivity of TMQ were determined by GC and GC-MS analyses (Table 1). The conversion of TMP was very low (Table 1, entry 1) with hypocrellins as the catalyst, although hypocrellins are photosensitizers.[19,20] On the

† Commercial TMP and TMQ from J&K were used. Hypocrellins were prepared as described previously;[21] $CuCo_2O_4$ was prepared according to a published procedure.[18] Organic solvents of analytical grade were used without additional purification.

To obtain 10 mol% HC/CCO, $CuCo_2O_4$ (1 g) was added to 20 ml of acetone and stirred for 0.5 h. Then, 100 ml of 1 g dm^{-3} hypocrellins acetone solution was dropped into the reaction system and stirred until the appearance of a colour of hypocrellins at room temperature. Finally, the mixture was distilled to remove the solvent.

The photocatalytic oxidation of TMP was carried out using a 100 ml three-necked flask equipped with a reflux condenser, a gas introduction tube and a magnetic stirrer. In a typical reaction, TMP (1 mmol), 50 mg of the 10 mol% HC/CCO catalyst and 50 ml of ethanol were placed in the flask, and then the mixture was irradiated with visible light (> 400 nm) and bubbled with air (about 10 ml min^{-1}). After 12 h, the reaction mixture was filtered and the catalyst was washed with ethanol. The products were analyzed by GC and GC-MS using authentic samples for comparison.

GC analyses were performed using a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector and a quartz capillary column (25 m×0.3 mm) filled with Carbowax 20M. GC-MS analyses of the products were carried out using an HP 5973/6890 system [electron ionization at 70 eV, He carrier gas, 30 m×0.25 mm cross-linked 5% PHME siloxane (0.25 μm coating) capillary column; HP-5MS] or a VG-7070 instrument. The UV-VIS spectrum of the catalyst was measured with a TU-1901 UV-VIS spectrophotometer using a 1 cm quartz cell.

Table 2 Influence of solvents.[a]

Entry	Solvent (amount/cm^3)	Conversion of TMP (mol%)[b]
1	—	0.0
2	Methanol (50)	1.3
3	Ethanol (10)	3.7
4	Ethanol (20)	4.9
5	Ethanol (30)	6.5
6	Ethanol (40)	7.0
7	Ethanol (50)	7.3
8	Ethanol (60)	7.3
9	Ethanol (100)	7.4
10	Acetone (50)	0.5
11	Chloroform (50)	1.0
12	Acetonitrile (50)	1.7
13	Dichloromethane (50)	1.2

[a]Reaction conditions are specified in Table 1. [b]In all experiments the selectivity of TMQ was 100%.

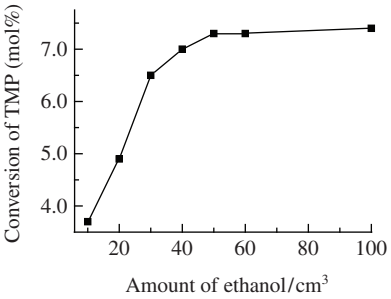


Figure 1 The effect of ethanol on the conversion of TMP.

other hand, TMP was not converted into TMQ using single $CuCo_2O_4$ as the photocatalyst (Table 1, entry 11) because $CuCo_2O_4$ did not absorb visible light.[18] Furthermore, no photooxidation took place in the absence of the catalyst (entry 12, Table 1) or without irradiation. The conversion of TMP was remarkably increased by the HC/CCO catalysts. Surprisingly, the TMP conversion decreased after the recycling of a high-ratio catalyst (Table 1, entries 8 and 10). However, the 10 mol% HC/CCO catalyst lost its photocatalytic activity under the same conditions. Simultaneously, hypocrellins were determined by GC-MS in the filtrate, implying hypocrellins desorbed from the catalyst. Moreover, the conversion of TMP was 1.4% in the absence of air (Table 1, entry 5); thus, singlet oxygen could be involved.

Table 2 and Figure 1 show the results of the study of reaction conditions using TMP as the substrate and 10 mol% HC/CCO as the catalyst in various solvents. Ethanol was found the best suitable solvent for the reaction (Table 2, entries 3–9). The conversion of TMP decreased in the order ethanol > acetonitrile > methanol > dichloromethane > chloroform > acetone > no solvent. The influence of solvents was consistent with our previous results of TMP oxidation using hypocrellins as the photocatalyst.[14]

Irradiation time is an important factor of photooxidation; the conversion of TMP affected by reaction time was investigated under the same conditions (Figure 2). The rate of TMP conversion increased with irradiation time (up to 12 h), and the selectivity for TMQ was constant (nearly 100%). More irradiation time did not contribute to the conversion of TMP.

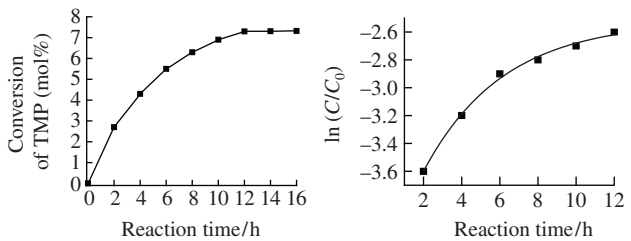


Figure 2 The effect of reaction time on the conversion of TMP.

Table 3 Recycling of catalyst.[a]

Run	Conversion of TMP (mol%)[b]
0 (fresh catalyst)	7.30
1	7.28
2	7.31
3	7.30
4	7.29
5	7.29

[a]Reaction conditions are specified in Table 1. [b]In all experiments the selectivity of TMQ was 100%.

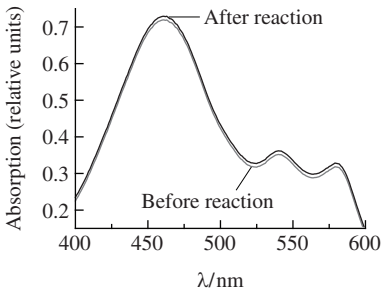


Figure 3 UV-VIS spectra of hypocrellins before and after reaction.

The catalyst was recycled in the following way: after the first photooxidation run with a fresh catalyst, it was filtered off and dried in a vacuum for 5 h; then, it was recharged to the flask for the subsequent run. This procedure was repeated five times (Table 3). To validate the leaching of hypocrellins, hypocrellins and $CuCo_2O_4$ were obtained from the 10 mol% HC/CCO catalyst using acetone as an isolating reagent. Then, the structure and amount of hypocrellins were verified by UV-VIS spectroscopy (Figure 3) to ensure that the catalyst remained unchanged in the reaction system.

This work was supported by the Natural Science Foundation of Yunnan Province (project nos. 2005C0078M and 2007B228M) and by the Special Fund from Key Subject of Yunnan Province (Organic Chemistry).

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Received: 25th December 2009; Com. 09/3442