Catal Lett (2008) 123:123–128
DOI 10.1007/s10562-008-9404-x

Selective Oxidation of Cyclohexane to Cyclohexanone Catalyzed by Phenanthroline–$CuCl_2$ Complex

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Received: 22 November 2007 / Accepted: 14 January 2008 / Published online: 14 March 2008

Abstract A highly efficient oxidation of cyclohexane to cyclohexanone is accomplished over phenanthroline–$CuCl_2$ catalyst in relatively mild conditions. This study realized nearly 100% selectivity for cyclohexanone at 24.4% conversion of cyclohexane. The reaction has been studied by various parameters like performance of copper(II) salts, effect of solvents, influence of bases, the ratio of *o*-phenanthroline: $CuCl_2$, and reaction time. In order to further study this reaction system, the possible mechanism was proposed.

Keywords Phenanthroline–$CuCl_2$ · Oxidation · Cyclohexane · Cyclohexanone

1 Introduction

The aerobic selective oxidation of hydrocarbons is a major goal of today's research in catalysis as selectively oxidized hydrocarbons can be used as feedstock for the preparation of fine chemicals [1–4]. Of particular importance is the oxidation of cyclohexane due to the large demand for its oxidized products such as cyclohexanone and cyclohexanol, which are important raw materials for the production of adipic acid and caprolactam [5]. In industry, the oxidation of cyclohexane is notoriously inefficient because it offers selectivities no higher than 80% even at 4% conversion [6, 7]. The greater demand for oxidation products of cyclohexane and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process. Many catalysts are extensively used [8–18], among which copper catalysts involving coreductants are most common. However, most of them show low selectivity of cyclohexanone or require higher temperature.

Phenanthrolines and phenanthroline–copper complexes are known for high activity for the oxidation of alcohols into aldehydes and ketones [19–22]. Recently, Xu et al. reported an interesting metal-free aerobic oxidation of cyclohexane to adipic acid and cyclohexanone using catalytic amounts of *o*-phenanthroline, NHPI and bromine [23]. However, it has not been sufficiently explored for the aerobic oxidation of cyclohexane employing phenanthroline–$CuCl_2$ (PCu) catalyst at room temperature. Herein we describe an efficient, aerobic catalytic system for the transformation of cyclohexane into cyclohexanone under mild conditions.

2 Experimental

2.1 Materials

All materials were of analytical grade. *o*-Phenanthroline, cyclohexane, cyclohexanone, cyclohexanol, methanol, ethanol, acetone, acetic acid, dichloromethane, chloroform, acetonitrile, sodium hydroxide, sodium carbonate, sodium bicarbonate, potassium hydroxide, potassium carbonate, potassium bicarbonate, and all copper salts were purchased from J&K Ltd. or China National Medicines Corporation Ltd.

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2.2 Physical Measurements

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 20 M. GC–MS analyses of the products were carried out using a HP 5973/6890 system (electron impact 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 catalyst was performed with a TU-1901 UV–Vis spectrophotometer using a quartz cell.

2.3 Preparation of Catalyst

About 0.25 mol *o*-phenanthroline was dissolved in 50 mL acetonitrile, and then the solution was transferred into 250 mL flask. About 0.25 mol copper salt was dissolved in 50 mL deionized water, and then the solution of copper salts was transferred into 250 mL flask. In order to insure the catalyst was fresh, the solution of *o*-phenanthroline and solution of copper salts must be mixed according to 2:1 ratio before reaction.

2.4 General Oxidation of Cyclohexane Catalyzed by Phenanthroline–$CuCl_2$ Complex

Oxidation reactions were performed in a stirring round bottom flask. Reactions were carried out at atmospheric pressure and room temperature (25 ± 3 °C) under open-wide system. Typically, 1 mmol cyclohexane in 5 mL of solvent and 2.5 mol% PCu was slowly added to the reaction flask with slow stirring. After a few minutes, 5% potassium carbonate was added to the reaction mixture at room temperature and open-wide system. The mixture was adjusted to acidity (pH 5–6) after 72 h and 10 mL fresh solvent was added. The organic phase was then subjected to GC and GC–MS analyses.

3 Results and Discussion

3.1 Performance of Different Copper(II) Salts

In order to test the efficiency of different copper(II) salts, the catalytic activity of various *o*-phenanthroline–copper salts has been examined for the aerobic oxidation of cyclohexane. The oxidation of cyclohexane was carried out with air (atmospheric pressure) in the presence of a catalytic amount of copper salts and *o*-phenanthroline in acetonitrile at room temperature. The conversion of cyclohexane and the selectivity of cyclohexanol and cyclohexanone were determined by GC analyses. The representative results for the catalytic activity of various *o*-phenanthroline–copper salts are shown in Table 1. From Table 1, we can see that nature of the copper counterion is critical to success of the reaction with Cl^-, Br^- and ClO_4^- proving to be the most effective conversion of cyclohexane, and Cl^- was particularly efficient in the selectivity of cyclohexanone. The effect of these copper counterions was similar with the reported research of Marko et al. [20]. The effect of copper salts was in the order of $CuBr_2 > Cu(ClO_4)_2 > CuCl_2 > Cu(OH)_2 > Cu(NO_3)_2 > Cu(OAc)_2 > CuSO_4$, indicating that a copper salt bearing a more basic or an electron donating ligand is suitable for the present oxidation. In addition, CuO and Cu powder also showed certainly catalytic activity (entries 8 and 9, Table 1) because they were converted to soluble copper salts during reaction system [10]. Considering the conversion of cyclohexane and the selectivity of cyclohexanone, we suggest that *o*-phenanthroline–$CuCl_2$ (PCu) is a suitable catalyst for the reaction system.

3.2 Effect of Various Solvents

To choose the best oxidation solvent in the presence of PCu as catalyst, the oxidation reactions were carried out in differently common solvents under the same conditions. The results were presented in Table 2. It was found that acetonitrile (entry 7, Table 2) provided the best oxidation medium for higher substrate conversion and selectivity of cyclohexanone. The observed differences from acetonitrile to acetone may be attributed to the difference in polarities of the solvent [24, 25]. It is interesting to note that acetonitrile was also used

Table 1 The effect of various copper salts

Entry	Catalyst	Conversion of cyclohexane (mol%)	Selectivity of cyclohexanol (mol%)	TON
1	$CuCl_2$	1.37	24	0.55
2	$CuBr_2$	1.41	37	0.56
3	$CuSO_4$	0.85	56	0.34
4	$Cu(NO_3)_2$	0.98	81	0.39
5	$Cu(OAc)_2$	0.88	85	0.35
6	$Cu(ClO_4)_2$	1.39	49	0.55
7	$Cu(OH)_2$	1.12	25	0.45
8	CuO	0.75	30	0.30
9	Cu power	0.25	74	0.10

Reaction conditions: 1 mmol cyclohexane, 2.5 mol% catalyst, solvent: 5 mL acetonitrile, reaction time: 72 h, reaction temperature: ambient temperature (25 ± 3 °C), oxidant: air

Table 2 The effect of solvents

Entry	Solvent (5 mL)	Conversion of cyclohexane (mol%)	Selectivity of cyclohexanol (mol%)	Selectivity of cyclohexanone (mol%)	TON
1	Methanol	0.74	45	55	0.29
2	Ethanol	0.81	49	51	0.32
3	Acetone	0.35	26	73	0.14
4	Acetic acid	1.06	11	67	0.42
5	Dichloro methane	1.11	46	54	0.44
6	Chloroform	1.29	32	68	0.52
7	Acetonitrile	1.37	24	76	0.55

Reaction conditions: 1 mmol cyclohexane, 2.5 mol% catalyst, solvent: 5 mL acetonitrile, reaction time: 72 h, reaction temperature: ambient temperature (25 ± 3 °C), oxidant: air

successfully for many copper-catalyzed oxidation reactions [26–28]. Furthermore, the volatility of acetonitrile is lower than that of other solvents under open-wide system, so the utilization factor of acetonitrile is more here than in others. On the other hand, this implied lower environmental contamination. All these implied acetonitrile was a suitable solvent for the oxidation of cyclohexane to cyclohexanone using PCu as catalyst under aerobic conditions.

3.3 Influence of Different Bases

During the course of our study of PCu in oxidation reactions of cyclohexane to cyclohexanone, we have found that the reactions were performed in basic media under aerobic conditions (Table 3). The conversion of cyclohexane and the selectivity of cyclohexanone in non-basic media are obviously lower than in basic media. A variety of other bases [KOH K_2CO_3 $KHCO_3$ NaOH Na_2CO_3 $NaHCO_3$ $CaCO_3$ $Ca(HCO_3)_2$ and $Ca(OH)_2$] were initially tested in this aerobic oxidation system. Surprisingly, none proved to be as efficient as K_2CO_3. In this reaction system, K_2CO_3 should act as a base and react with the HCl formed during the initial replacement of the chloride ligand by the cyclohexane [29]. On the other hand, K_2CO_3 could act as a dehydrating agent in the oxidation reaction. It suggested that K_2CO_3 was an optimal base in the oxidation of cyclohexane to cyclohexanone.

3.4 Effect of the Ratio of *o*-Phenanthroline and $CuCl_2$

We consider copper(II) salts can form hexa-complexation with ligand. At the same time, in order to investigate the effect of various *o*-phenanthroline–$CuCl_2$ ratios, we examined the effect of the ratio of *o*-phenanthroline and $CuCl_2$ using cyclohexane as the substrate in acetonitrile under ambient conditions. Some of the obtained examples are presented in Table 4. As shown in Table 4, the conversion of cyclohexane, cyclohexanol and cyclohexanone selectivities was hardly changed from 1:1 to 1:3 ratio of *o*-phenanthroline: $CuCl_2$. The result implied that cyclohexane would be oxidized to cyclohexanol and cyclohexanol only by *o*-phenanthroline–$CuCl_2$ not $CuCl_2$. In addition, the selectivity of cyclohexanone was not reach

Table 3 The influence of bases

Entry	Base (two equivalents)	Conversion of cyclohexane (mol%)	Selectivity of cyclohexanol (mol%)	selectivity of cyclohexanone (mol%)	TON
1	–[a]	1.37	24	76	0.55
2	KOH	23.9	10	90	9.56
3	K_2CO_3[b]	24.3	7	93	9.72
4	K_2CO_3	24.4	0	100	9.76
5	K_2CO_3[c]	24.4	1	99	9.76
6	$KHCO_3$	24.1	16	84	9.64
7	NaOH	17.8	13	87	7.12
8	Na_2CO_3	18.0	17	83	7.20
9	$NaHCO_3$	17.9	18	82	7.16
10	$CaCO_3$	13.2	21	79	5.28
11	$Ca(HCO_3)_2$	13.0	19	81	5.20
12	$Ca(OH)_2$	12.9	15	85	5.16

Reaction conditions: 1 mmol cyclohexane, 2.5 mol% catalyst, two equivalent of base, solvent: 5 mL acetonitrile, reaction time: 72 h, reaction temperature: ambient temperature (25 ± 3 °C), oxidant: air

[a] No base

[b] One equivalent of K_2CO_3

[c] Three equivalents of K_2CO_3

Table 4 The effect of the ratio of *o*-phenanthroline and $CuCl_2$

Entry	*o*-Phenanthroline: $CuCl_2$	Conversion of cyclohexane (mol%)	Selectivity of cyclohexanol (mol%)	Selectivity of cyclohexanone (mol%)
1	3:1	1.9	0	100
2	2:1	24.4	0	100
3	1:1	23.1	27	73
4	1:2	23.3	26.8	73.2
5	1:3	23.2	27	73

Reaction conditions: 1 mmol cyclohexane, solvent: 5 mL acetonitrile, two equivalents of K_2CO_3, reaction time: 72 h, reaction temperature: ambient temperature (25 ± 3 °C), oxidant: air

at 100% under inadequate *o*-phenanthroline. The selectivity of cyclohexanone was 100% when the ratio of *o*-phenanthroline: $CuCl_2$ exceeded 2:1. The conversion of cyclohexane, however, was lowest because of unformed peroxide due to the hydroxy would not be complex with copper ion under hexa-complexation of *o*-phenanthroline–$CuCl_2$ (Fig. 3C).

3.5 Effect of Reaction Time

We have found that the conversion of cyclohexane was affected by reaction time under the same conditions (Fig. 1). It can be found that the rate of cyclohexane conversion increased with increase in reaction time up to 72 h, and the selectivity of cyclohexanone was constant (nearly 100%). More reaction time did not contribute to the selectivity of cyclohexane. From Fig. 1, we also found that the non-linear increase of cyclohexane conversion was puzzling. To investigate the reason, we studied the UV–Vis spectrum of catalyst (Fig. 2). The absorption spectrum of from 400 to 300 nm implied peroxide was formed in reaction system [30, 31]. The absorption spectrum from 800 to 600 nm indicated $[Cu(phen)_2OH]^+OH^-$ was formed under ambient conditions (Fig. 3b) [32]. Moreover, The absorption spectrum of from 400 to 300 nm appeared in 1 h during the reaction. The position of the absorption peak was not changed with reaction time after 1 h, although the concentration of peroxide was still diverse. This implied that the non-linear conversion of cyclohexane could be related to the formation and amount of peroxide.

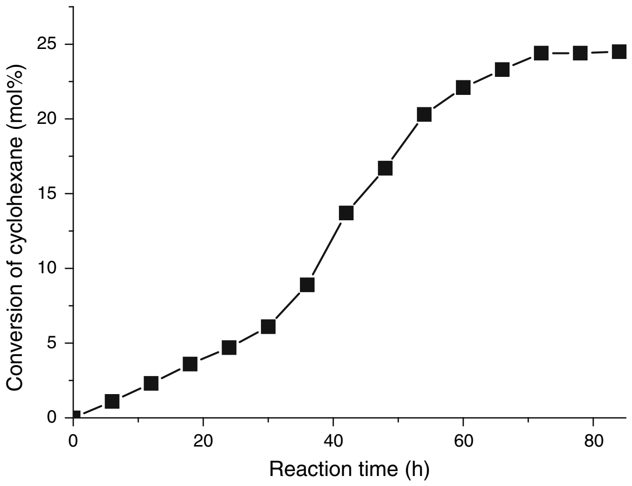


Fig. 1 The effect of reaction time (reaction conditions: 1mmol cyclohexane, solvent: 5 mL acetonitrile, two equivalents of K_2CO_3, reaction temperature: ambient temperature (25 ± 3 °C), oxidant: air)

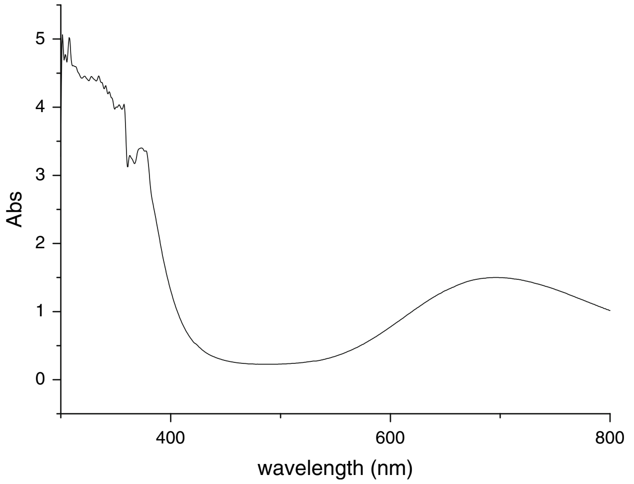


Fig. 2 UV–Vis spectra of PCu (*o*-phenanthroline: $CuCl_2 = 2:1$)

3.6 Possible Mechanism

Mechanistic studies of cyclohexane oxidation with *o*-phenanthroline–$CuCl_2$ complex catalyst showed that, under ambient conditions, the catalyst precursor was a $[Cu(phen)_2OH]^+OH^-$ (phen = *o*-phenanthroline) (Fig. 4). According to the UV–Vis spectrum of the catalyst and Refs. [19–22, 30–32], we propose the possible mechanism as follows: First, $[Cu(phen)_2OH]^+OH^-$ **1** could be oxidized to $[Cu(phen)_2OOH]^+OH^-$ **2** under aerobic conditions, and then an initial hydroxy-transfer reaction with $[Cu(phen)_2OOH]^+OH^-$ generated cyclohexyl oxide **3** and one equivalent of H_2O. Upon reaction with oxygen, **3** then produced the cyclohexyl peroxide **4**. Homolytic cleavage of **4** occurred to generate cyclohexanone, regenerate the loaded catalyst **1**, and initiate a second catalytic cycle (Scheme 1).

4 Conclusion

In summary, a highly efficient oxidation of cyclohexane to cyclohexanone is accomplished over *o*-phenanthroline–$CuCl_2$ catalyst in relatively mild conditions. This study

Fig. 3 *o*-Phenanthroline–$CuCl_2$ complexes formed under different ratios

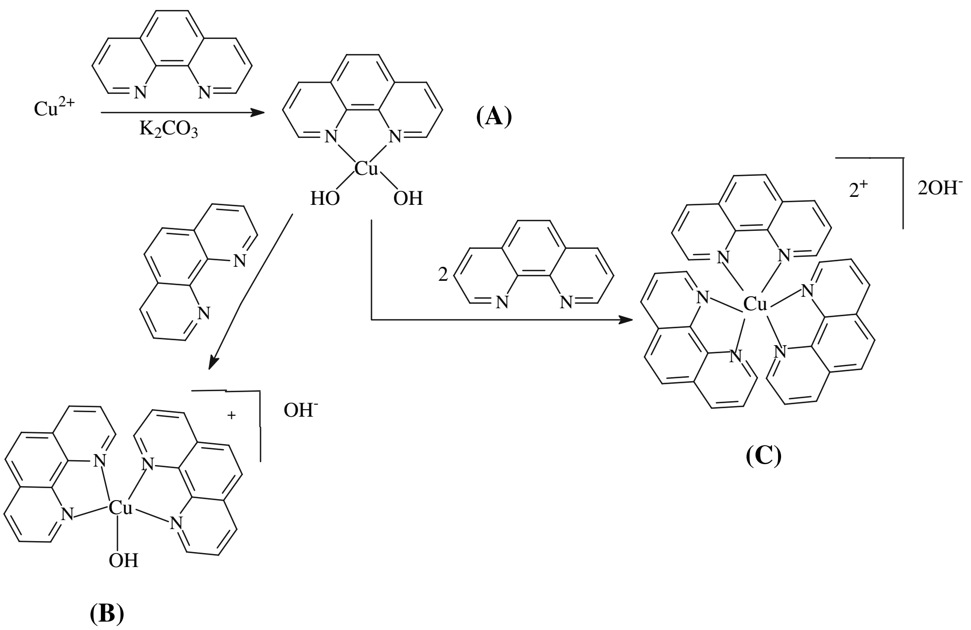
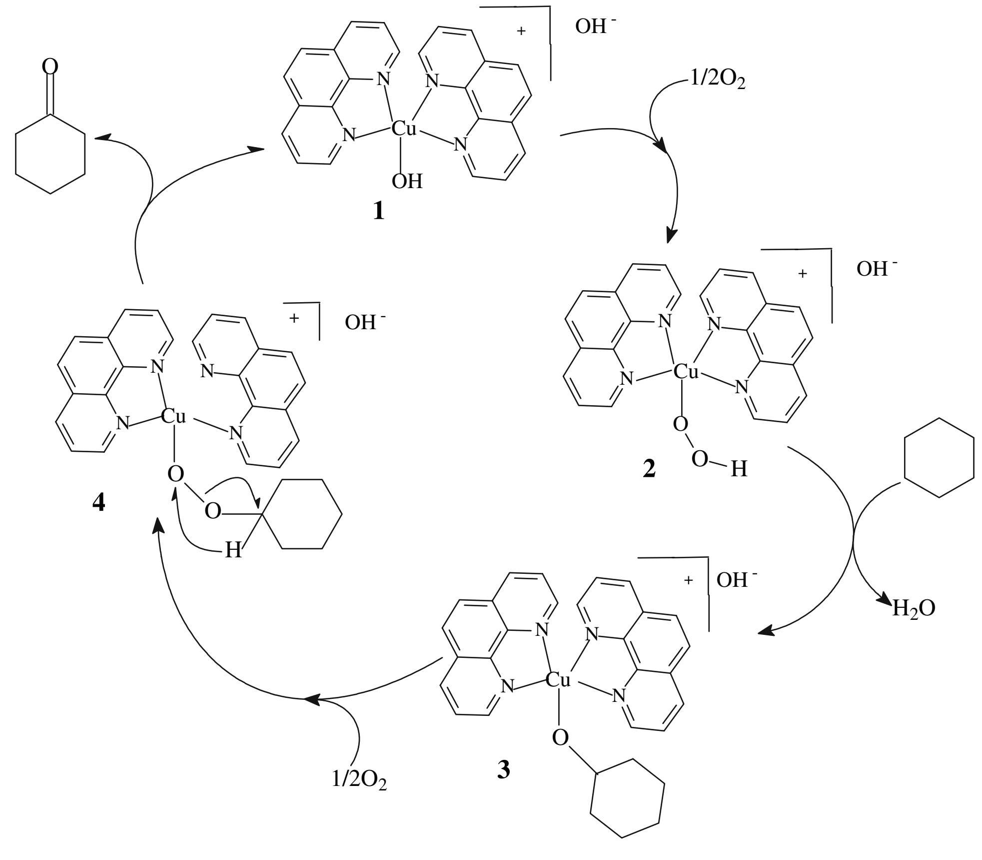
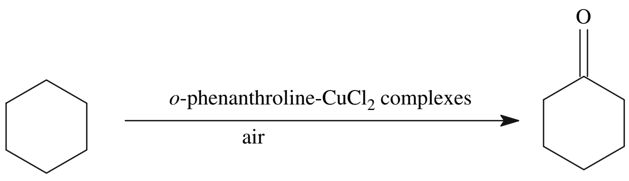


Fig. 4 The catalytic cycle proposed for cyclohexane with *o*-phenanthroline–$CuCl_2$ complexes under ambient conditions





Scheme 1

realized nearly 100% selectivity for cyclohexanone at 24.4% conversion of cyclohexane under aerobic conditions. The rate of cyclohexane and the selectivity of cyclohexanone largely depended on the experimental conditions. In addition, the present method for selective oxidation cyclohexane to cyclohexanone has an obvious advantage over conventional methods that only air, inexpensive *o*-phenanthroline and readily available $CuCl_2$ were used. Further investigations are in progress.

Acknowledgment This research was supported by the Natural Science Foundation of Yunnan Province (Project 2005c0078M, and 5Z0521C).

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