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Cataliticoxidation of benzyl alcohol by Cu(II) polypyridyl complexes

Ghobad Mansouri

Department of Chemistry, Payame Noor University (PNU), P.O. BOX 19395-3697, Tehran, Iran

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Abstract

Two polypyridyl copper(II) complexes, [Cu(phen)(phen-dione)Cl]Cl (1) and [Cu(bpy)(phen-dione)Cl]Cl (2), (where Phen =1,10-phenanthroline, bpy =2,2'-bipyridine and Phen-dione = 1,10-phenanthroline-5,6-dione), were used as efficient catalysts for the oxidation of benzyl alcohol to benzaldehyde. The effects of various parameters such as reaction temperature, reaction time, etc. were studied. The catalysts were stable at the operation conditions and recyclable. The conversion percentage for complex **1** was higher than the complex **2**.

Keywords: Copper(II) complex; benzyl alcohol; aldehyde; catalytic oxidation.

Introduction

Oxidation reactions play an important role in synthetic chemistry and provide important methodology for the introduction and modification of functional groups. A large number of coordination complexes are able to undergo redox reactions and catalyse the homogeneous and heterogeneous reactions [1-4]. Catalysts based on coordination complexes are very efficient for many chemical reactions due to their correct stability, variety of oxidation states, different geometries, coordination modes, and variety of ligands [5-17]. Electronic and steric parameters of coordination complexes play a key role in the catalytic performance [18-22].

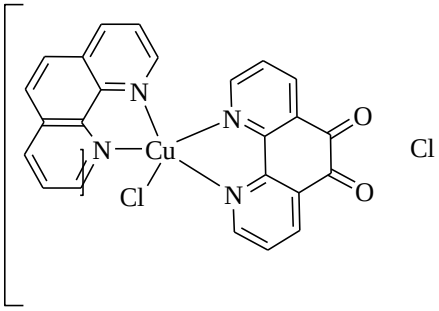
The oxidation of aliphatic and aromatic alcohols into corresponding aldehydes, ketones or acides is a fundamental process in the lab-scale and industrial plants [23,24].

Coordination complexes of vanadium, molybdenum, titanium, tungsten, ruthenium, osmium, cobalt, platinum, palladium, copper and iron have been studied as catalysts for oxidation reactions with hydrogen peroxide as an oxidant [25-31].

Polypyridyl copper (II) complexes have a significant catalytic activity in oxidation reactions[32-39].

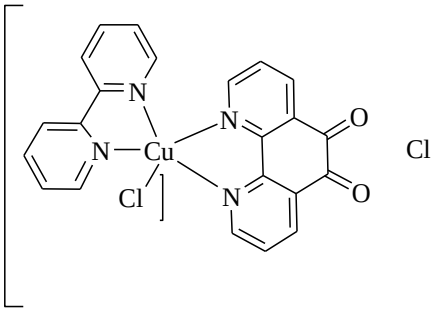
Here we reported a novel environmentally friendly oxidation process for the oxidation of benzyl alcohol using copper (II) complexes (Schemes 1 and 2) and H_2O_2 under solvent free conditions.

*Corresponding author: Ghobad Mansouri
Tel: +98 (84) 32221052, Fax: +98 (84) 32221053
E-mail: mansouri.gh@gmail.com



[Cu (phen)(phen-dione)Cl]Cl

(Scheme 1)



[Cu (bpy)(phen-dione)Cl]Cl

(Scheme 2)

Materials and characterization

All chemicals and solvents were obtained from commercial sources and used as received. Hydrogen peroxide (H_2O_2, 30% in water) was titrated by the iodometric method before use. Elemental analyses were performed using a Heraeus CHN-O-Rapid elemental analyzer. FT-IR spectra were recorded as KBr pellets on a FT-IR JASCO - 460 spectrophotometer in the spectral range 4000-400 cm^{-1}. Chromatographic analyses were carried out using a Varian 3400 gas chromatograph with a capillary column and FID detector.

Synthesis of the complexes

The copper complexes, [Cu(phen)(phen-dione)Cl]Cl (**1**) and [Cu(bpy)(phen-dione)Cl]Cl (**2**), were synthesized according to the literatures [40].

[Cu(phen)(phen-dione)Cl]Cl: Green solid. Elemental analysis calculated for $C_{24}H_{14}N_4O_2Cl_2Cu$: C, 54.92; H, 2.68; N, 10.67%. Found: C, 54.98; H, 2.61; N, 10.72%. IR (KBr): υ (cm^{-1}) 3081, 2924, 1699, 1578, 1519, 1429, 1297, 1023, 839, 724.

[Cu(bpy)(phen-dione)Cl]Cl: Light green solid. Elemental analysis calculated for $C_{22}H_{14}N_4O_2Cl_2Cu$: C, 52.76; H, 2.81; N, 11.18%. Found: C, 52.73; H, 2.84; N, 11.21%.IR (KBr): υ (cm^{-1}) 3087, 2985, 1706, 1600, 1576, 1429, 1300, 1029, 838, 765.

Oxidation of benzyl alcohol

The oxidation of benzyl alcohol was carried out in a 25 mL two-naked round bottom flask equipped with a reflux condenser and magnetic stirrer using Cu(II) complexes (**1** and **2**) as catalysts. Benzyl alcohol (1 mL) and 30% H_2O_2 (1, 2 and 3 mL) were mixed and an appropriate amount of the catalyst (0.0125, 0.025 and 0.050 g) was added and the reaction mixture was heated at 100 ºC for 24 h. The progress of the reaction was monitored using gas chromatography by withdrawing aliquots of the reaction mixture at regular time intervals. The Cu(II) complexes were extracted from the reaction mixture by 5 mL of distilled water. The products were identified by GC and FT-IR and were compared with the commercially available carbonyl compounds. Also, 2,4-dinitrophenylhydrazine (DNPH) test was used as an evidence to identify the benzaldehyde as product.

Blank tests were performed under typical reaction conditions in the absence of Cu (II) complexes (catalysts) and shown the formation of only minor amounts (5%) of benzaldehyde.

Results and discution

In order to evaluate the catalytic activities of the polypyridyl Cu(II) compounds, complexes **1** and **2** were prepared according to our previous paper and characterized by infrared spectroscopy and elemental analyses. The results were matched with the

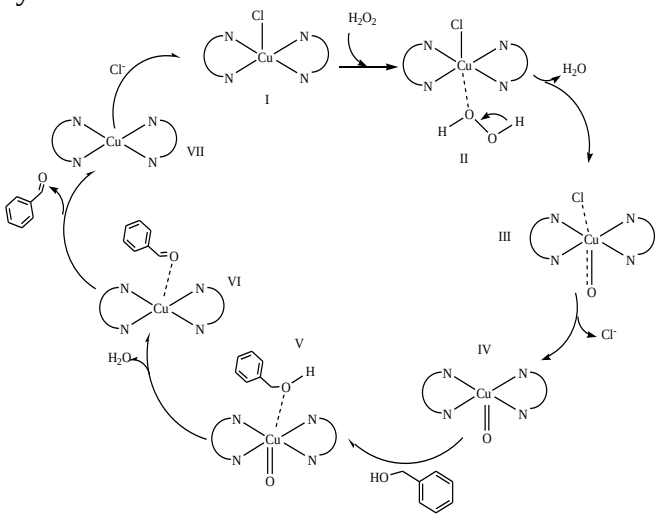
structures described previously for these complexes [40].

All reactions were done in optimum conditions, at 100 ºC temperature for 24 h with 0.025 g of catalysts, 3 mL H_2O_2 (30 %) and 1 mL of benzyl alcohol. Catalysts **1** and **2** showed 52 % and 48 % conversion of benzyl alcohol, respectively. Furthermore, in the absence of catalyst, no significant amount of benzaldehyde was produced (Table 1).

The FT-IR spectrum of products clearly exhibit bands at 1703 and 1710 cm^{-1} that are ascribable to a stretching frequency of the C=O band of benzaldehyde. This bond was not seen inreagent and showed the oxidation of benzyl alcohol. The addition of DPNH to resulting solution gave an orange precipitate. The formation of this precipitate was a positive test for the production of benzaldehyde.

Effect of the amount and nature of the catalyst

The catalyst amounts were varied from 0.0125 g to 0.0500 g for the reaction carried out at 100 ºC for 24 h while the other reaction conditions were remaining constant. The results are shown in Table 1. The conversion of benzyl alcohol to benzaldehyde increases by raising the amount of catalysts. These results demonstrate clearly that Cu(II) complexes (**1** and **2**) are very active in the oxidation reaction and that even a small amount of the complexes (0.025 g) can lead to a significant conversion. The geometry of five-coordinate Cu(II) complexes are generally trigonal bipyramidal [40]. In the complexes **1** and **2**, the presence of a monodentate chloro ligand, the ability of the complexes to possess coordination number of 4 or 6 and the rigidity of the polypyridyl ligands are significant factors in the catalytic activity. In view of these proposed structures, the complexes contain open coordination sites for the oxidant (H_2O_2), thus replacing the H_2O molecules and binding directly to the central metal ion (Cu^{2+}). This allowed oxygen to be transferred from H_2O_2 to Cu^{2+}[41](Scheme 3). Also, these complexes are more susceptible to suffer a rapid electron transfer. Table 1 shows the conversion percentage of the reaction with complex **1** which is higher than complex **2**. In fact, high activity of complex **1** is due to the facilitation of the electron transfer rate as increased in the case of phen ligand. Furthermore, the higher stability of phenantheroline complex may prevent the decomposition of the complex during the catalytic cycle.



Scheme 3. Proposed mechanism of catalytic oxidation by Cu(II) complexes.

Table 1. Effect of the amount the copper(II) complexes (**1** and **2**) on the catalytic oxidation.

Catalyst	Amount (g)	Conversion (%)
1		5
1	0.0125	38
1	0.025	52
1	0.05	33
2		5
2	0.0125	32
2	0.025	48
2	0.05	30

Effect of H_2O_2 concentration

In order to determine the effect of H_2O_2 on the oxidation of benzyl alcohol to benzaldehayde, three different benzyl alcohol to H_2O_2 ratio (1:1, 1:2 and 1:3 mL) were investigated while the other parameters including catalyst (0.025 g), temperature (100 ºC) and reaction time (24 h) were kept fixed. The results (Table 2) show that when H_2O_2 and alcohol ratio was 3:1 mL, the optimum conversion was of 52 % (for **1**) and 48% (for **2**).

Table 2. Effect of H_2O_2 on the oxidation of benzyl alcohol to benzaldehayde.

Catalyst	H_2O_2 (mL)	Conversion (%)
1	1	30
1	2	32
1	3	52
2	1	27
2	2	30
2	3	48

Effect of reaction time

The time dependence of the catalytic oxidation of benzyl alcohol (Figure 1) was studied performing the reaction of benzyl alcohol, 30% H_2O_2 (3 mL) and catalyst (0.025 g) at 100 ºC in a two-naked round bottom flask. The samples were drawn out at regular intervals and analyzed by GC. Figure 1 shows that the conversion of benzyl alcohol increases as time increases and then remains constant.

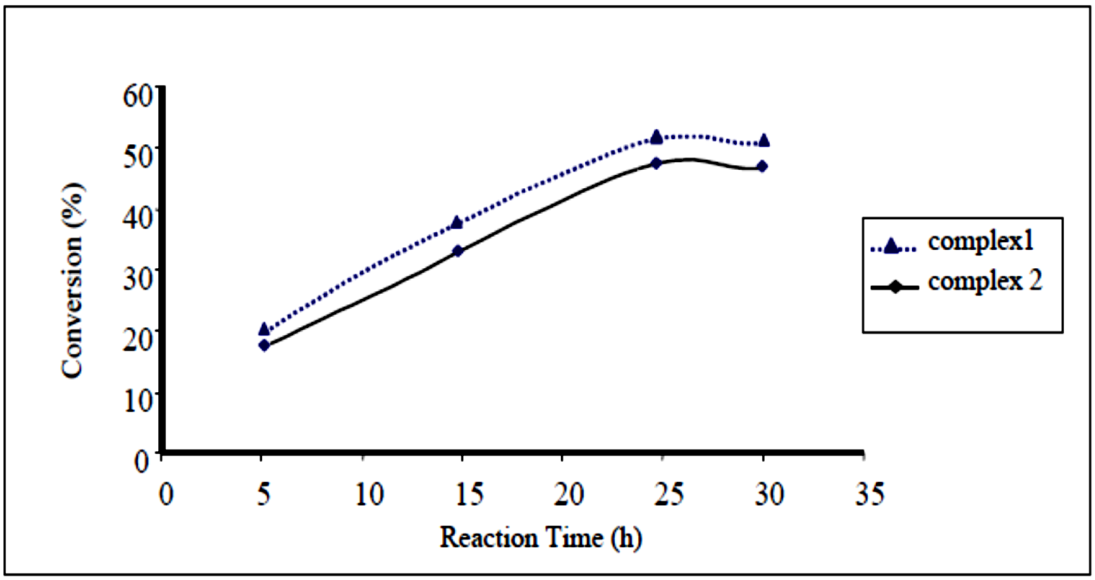


Figure 1. Time dependence of the catalytic oxidation of benzyl alcohol with the Cu(II) complexes.

Effect of temperature

The effect of temperature on the oxidation of benzyl alcohol using (0.025 g) Cu(II) complexes (**1** and **2**) as catalyst and (3 mL) 30% H_2O_2 were investigated at three different temperatures viz. 50, 100 and 150 ºC. The improvement in conversion was observed on increasing the temperature from 50 to 100 ºC, so that a temperature of 100 ºC was considered to be optimum (Figure 2).

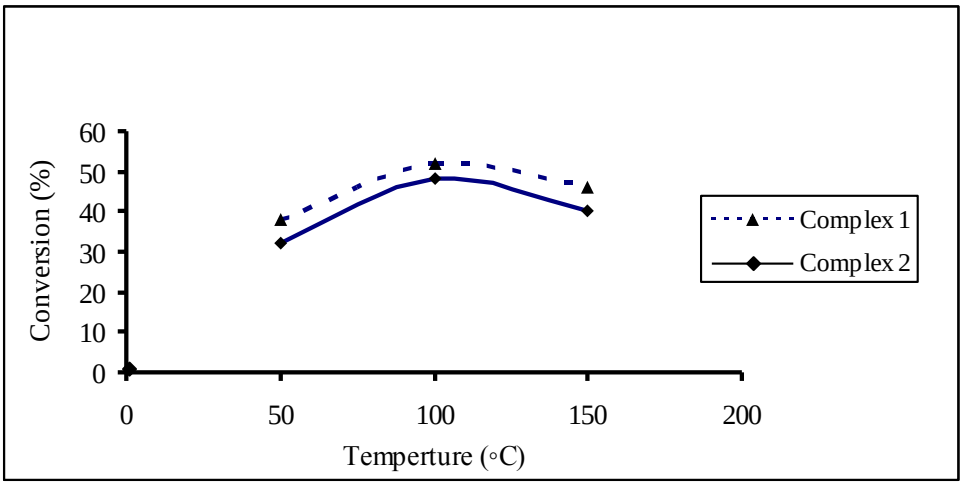


Figure. 2. The effect of temperature on the oxidation of benzyl alcohol

Conclusion

In this study, we have demonstrated, for the first time, the catalytic activity of the polypyridyl Cu(II) complexes (**1** and **2**) for the oxidation of benzyl alcohols in the presence of H_2O_2 and solvent free conditions. The reaction parameters were optimized. In addition, The catalyst can be recycled and also these byproducts are environmentally friendly. These catalyst systems are actived and suitable for oxidation of benzyl alcohol.

Acknowledgments

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