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Publisher *Taylor & Francis*

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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Catalytic Oxidation Reaction. Oxidation of Cyclohexene Catalyzed by Copper-Polymer-Bound 2,2'-Bipyridine Complexes

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**To cite this Article** Lei, Z. Q. and Wang, Y. P.(1992) 'Catalytic Oxidation Reaction. Oxidation of Cyclohexene Catalyzed by Copper-Polymer-Bound 2,2'-Bipyridine Complexes', *Journal of Macromolecular Science, Part A*, 29: 11, 321 – 324

**To link to this Article:** DOI: 10.1080/10101329208054597

**URL:** <http://dx.doi.org/10.1080/10101329208054597>

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**CATALYTIC OXIDATION REACTION. OXIDATION OF CYCLOHEXENE  
CATALYZED BY COPPER-POLYMER-BOUND 2,2'-BIPYRIDINE  
COMPLEXES**

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**ABSTRACT**

Cyclohexene **1** was oxidized with 1 atm. of oxygen or air in the presence of copper-polymer-bound 2,2'-bipyridine-L [where L = 0, 1, 10-phenanthroline (phen), triphenyl phosphine (Pph<sub>3</sub>), and 2,2'-bipyridine (bipy)] complexes at 60°C to give 2-cyclohexen-1-ol **2** and 2-cyclohexen-1-one **3** with the conversion ranging from 15%~40% and the total selectivity of **2** and **3** ranging from 85.2%~95.7% with the different complexes employed as catalyst. The change numbers [conversion of **1** (moles) per mol catalyst] of these complexes were all mount to over  $2.5 \times 10^3$  for 5h in the oxidation of cyclohexene with molecular oxygen.

**INTRODUCTION**

Cyclohexene was oxidised in the presence of copper catalyst such as PdCl<sub>2</sub>/CuCl [**1**], copper (I) ketenide [**2**], Cu(OAc)<sub>2</sub>/LiCl [**3**] and copper(II)/iodosylbenzene [**4**]. Some of the cited work need a special oxidants such as peroxide, which results in the difficult in analyzing and separating the products, or need carried out in aqueous solution, which, from the point of view of synthetic utility, suffers from the drawback of low solubility of most organic substrates.

We describe here a series of polymer-bound 2,2'-bipyridine-copper-L (where L = 0, phen, Pph<sub>3</sub>, and bipy) complexes and their catalytic properties in the oxidation of cyclohexene **1**. The oxidation were carried out under 1 atm. of oxygen or air in the absence of solvent at 60°C affords 2-cyclohexen-1-ol **2**, 2-cyclohexen-1-one **3** and cyclohexanone **4**. **2** and **3** were the major products in each case.

These polymer-supported copper(II) complexes are found to be the active catalysts for the oxidation of **1** and the efficient molecular oxygen activating agent somewhat like oxyhemocyanin [5~6].

## EXPERIMENTAL

## Polymer-bound 2,2'-Bipyridine (polymer-bipy)

Polymer-bipy were prepared in the general procedure based on the method described in the literature [7]. We modified the method by substituted bromination catalyst  $AlCl_3$  with iron powder and polystyrene-2% divinylbenzene with linear polystyrene (MW, 130000~150000). The polymer-bipy prepared by literature method contains one bipyridyl group for each seven to eight phenyl residues [7], but that prepared by modified method contains one functional bipyridyl group for each three to four phenyl residues [8].

## Preparation of Copper(II)-Polymer-bipy-L Complexes

Examples of copper(II)-polymer-bound 2,2'-bipyridine complex have been reported [7,9]. We prepared the polymer-supported-copper complexes according to the following procedure.

Copper chloride ( $CuCl_2 \cdot H_2O$  0.15g, 0.98mmol), polymer-bipy (0.3g, N, 1.59mmol) and L [(1) L=0; (2) L=phen, 0.2g, 1.00mmol; (3) L=Pph<sub>3</sub>, 0.5g, 1.91mmol; and (4) L=bipy, 0.15g, 0.95mmol] were added to 50ml THF-ethanol(1:1, V/V) mixed solvent, the mixture was heated and refluxed for 3h. The resulting polymer-supported complexes were isolated by filtration and were thoroughly washed with ethanol and benzene, dried in vacuum. The blue copper-polymer-bound 2,2'-bipyridine-L complexes were obtained. The amount of copper in the complexes (1)–(4) was 1.2%, 2.2%, 1.7% and 2.0% respectively (analyzed by ICP).

The polymer-supported complexes (1)–(4) were characterized by X-ray photoelectric spectroscopy (XPS). The results were shown in TABLE I.

Oxidation products were analyzed on a SHIMADZU QP-1000A GC/MS system.

## RESULTS AND DISCUSSION

## XPS Analysis Results and Discussion

TABLE I  
XPS Data for Complexes (1)–(4) and Polymer-bipy

Substrate	XPS peak	Binding energy (eV)	$\Delta Eb$ (eV)
$CuCl_2$	$Cu(2p_{3/2})$	934.2(EK 915.4)	0.0
(1)	$Cu(2p_{3/2})$	932.2(EK 915.2)	-2.0
	N(1s)	399.7	+1.0
(2)	$Cu(2p_{3/2})$	933.2(EK 915.8)	-1.0
	N(1s)	399.1	+0.4
(3)	$Cu(2p_{3/2})$	932.9(EK 915.3)	-1.3
	N(1s)	399.0	+0.3
	P(2p)	131.2	
ph <sub>3</sub> PO	P(2p)	132.5	
(4)	$Cu(2p_{3/2})$	932.4(EK 915.6)	-1.8
	N(1s)	399.5	+0.8
Polymer-bipy	N(1s)	398.7	0.0

**TABLE 2**  
Oxidation of Cyclohexene Catalyzed by Different  
Copper (II)-Polymer-Supported Complexes

Cat.	Oxidant	Conversion (mol %)	Product Selectivity (%) to <b>2</b> and <b>3</b>
(1)	O <sub>2</sub>	20	91.2
	air	15	92.7
(2)	O <sub>2</sub>	40	85.2
	air	31	88.7
(3)	O <sub>2</sub>	25	93.6
	air	18	95.7
(4)	O <sub>2</sub>	27	85.9
	air	20	86.5

Reaction condition: Cat. Cu, 0.0015mmol, cyclohexene 25mmol, 1 atm., 5h at 60°C

**TABLE 1** show that Cu(2p<sub>3/2</sub>) binding energy in complexes (1)–(4) were decreased 2.0eV, 1.0eV, 1.3eV and 1.8eV respectively compared with that in CuCl<sub>2</sub>. The N(1s) binding energy in complexes (1)–(4) increased 1.0eV, 0.4eV, 0.3eV, and 0.8eV respectively compared with that in polymer-bipy. This result shows that the charge on the copper atoms increased and that on the nitrogen atoms decreased when copper (II) was coordinated with polymer-bipy and L. This also indicates that the charge was transferred from nitrogen atoms to copper atoms in the complexes. The P(2p) binding energy in the complex (3) was 131.2eV, this shows that Pph<sub>3</sub> was not oxidized to ph<sub>3</sub>PO [in which P(2p) binding energy was 132.5eV] in the complex.

#### Oxidation results and Discussion

Oxidation of cyclohexene **1** catalyzed by complexes (1)–(4) in the presence of molecular oxygen affords 2-cyclohexen-1-ol **2** and 2-cyclohexen-1-one **3** as the major products. The results were listed in **TABLE 2**. Comparison of the relative efficiencies of (1)–(4) as catalysts for the oxidation of **1** were carried out. Complex (2) is a more efficient catalyst for the formation of **2** and **3** than complexes (1), (3) and (4). Oxidation of **1** by 1 atm. of oxygen with complexes (1)–(4) under the same condition provided conversion of 20mol%, 40mol%, 25mol% and 27mol% (based on the **1**) with the selectivity total of **2** and **3** of 91.2%, 85.2%, 93.6% and 85.9% respectively. Low conversions were obtained when the reactions were carried out in 1 atm. of air.

**TABLE 3**  
Oxidation of cyclohexene in Different Solvent

Solvent	Conversion(mol%)	Selectivity to 2 and 3 (%)
—	40	85.2
benzene	5	97.0
o-nitrobenzene	trace	98.8
HAc-NaAc(pH $\approx$ 7)	trace	99.0
Water	—	—
50% CTAB	trace	92.3

Reaction condition; Cat. (2). Cu, 0.0015mmol, cyclohexene 25mmol, solvent 5ml, 5h at 60°C.

The influence of solvent to the catalytic activity and selectivity was investigated. The results have shown in TABLE 3. Significantly low conversions were obtained when the reactions were carried out in o-nitrobenzene, HAc-NaAc buffer solution (pH $\approx$ 7), water and 50% CTAB solution. In aqueous solution, the low solubility of 1 holds back the catalytic activity. When the oxidation reaction was examined in benzene or o-nitrobenzene in which 1 is soluble, the catalytic conversion is still low. This result shows that low solubility is not the only factor that influences the catalytic activity of these complexes.

The oxidative cleavage of C—C bonds was found in the reaction. Side products were mainly organic acid, alcohol, ketone, aldehyde, produced from the oxidative cleavage of C—C bonds. Increase of side products was observed with the prolonged reaction time.

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