CHEMISTRY LETTERS, pp. 499-502, 1979. Published by the Chemical Society of Japan

OLIGOMER CATALYST. SPECIFIC OXIDATION OF PHENOLS CATALYZED BY OCTAMERIC OLIGO[1-(N-PHENYLCARBAMOYL)-AZIRIDINE] - COPPER COMPLEX

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Oxygen-oxidation of 2,6-xylenol, catalyzed by new type of oligomer complex from copper salt and octameric oligo[1-(N-phenylcarbamoyl)-aziridine] and its thio-analog, gives C-O coupling product in reasonable yield without forming C-C coupling product. This oligomer catalyst system was extended to the oxidation of several phenols such as 2,6-dimethoxyphenol, 2,6-di-t-butylphenol, 2,4-xylenol, and so on.

A large number of copper catalysts[1] for oxidation of phenols have been prepared. Some of them have been shown to possess very interesting catalytic activities, and recognized to be models for copper-containing enzymes such as laccase, tyrosinase, and so on. In particular, several polymer-copper catalysts[2] exhibit characteristic behaviors which differ largely from corresponding small ligand-copper catalysts. It may be due to the special structure and property of polymeric ligand.

Recently several authors[3] emphasized the remarkable properties of oligomer-metal complexes, but a little attention has been paid for development of their catalytic activities especially for redox reaction. We have already confirmed[4,5] that octameric oligo[1-(N-phenylcarbamoyl)-aziridine], $[CH_2CH_2N(CONHPh)]_{\underset{\sim}{8}}$[6] (oligo(NPCA)), and its thio-analog, oligo[1-(N-phenylthiocarbamoyl)-aziridine], $[CH_2CH_2N(CSNHPh)]_{\underset{\sim}{8}}$ (oligo(NPTCA)), show high specificity in the binding of Cu^{2+} and Hg^{2+} ions. This specificity differs from its monomer or from polymer. These previous findings encouraged us to investigate the properties and applications of oligomer-copper complex as catalyst.

In this communication, the oxidative coupling of phenol in the presence of oxygen was examined by using oligo(NPCA) or oligo(NPTCA)-copper catalyst. The binding features of oligomers are adequate for the use as oligomeric ligand of metal catalyst.

A homogeneous and green solution of oligo(NPCA)-copper complex is prepared by adding copper salt to the benzene-methanol soultion of oligo(NPCA)[7]. This complex has coordination number of 4 based on mole ratio method, and we used the complex with a mole ratio [>NCONHPh]/[Cu salt] 4 as catalyst in the following experiments.

2,6-Xylenol was oxidized effectively by using oligo(NPCA)-copper catalyst. The results are summarized in Table I, in which the results by using some analogs having similar urea structure are included for comparision. There are remarkable differences in the catalytic activities, indicating that the ligand circumstance in which copper ion is incorporated is a critical factor to cause the different activities. The spatial situation of ligands must be considered and oligo(NPCA) has some favorable features in the formation of catalytically active complex. The oxidation yields

Table I. Oxidation of 2,6-Xylenol with Copper Complex[a]

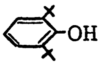
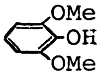
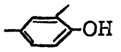
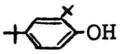
Ligand	[Ligand]/[Copper]	Solvent[b]	Time(hr)	Conversion(%)[c]
Oligo(NPCA)	1.1	A	4	9
	2.2	A	4	18
	4.0	A	4	23
		A	20	84
		B	4	12
	12.0	A	4	18
Oligo(NPTCA)	4.0	B	3	35
		B	10	94
Ureanized PEI[d]	4.0	B	4	0
	4.0	B	4	4
$Et_2NCONHPh$	4.0	B	4	1
Pyridine	4.0	A	4	23

(a) Oxidation conditions: 2,6-Xylenol concentration, 0.052 M. Concentration of $CuCl_2$, 0.0011 M. Under O_2 atmosphere at room temperature. (b) Solvent system: A, Benzene-MeOH (65:35, v/v) 10 ml. B, Benzene-MeOH-DMSO (64:35:1) 10 ml. (c) Conversion was calculated from GC and GPC analyses. (d) Ureanized PEI was prepared by polymer reaction of commercial polyethylenimine with phenylisocyanate. see ref. 4.

catalyzed by oligo(NPCA)-copper complex exhibit a maximun in a region where mole ratio of urea unit to copper ion is about 4. This suggests that the oligomer-copper complex, having coordination number of 4 as mentioned above, is catalytically most active.

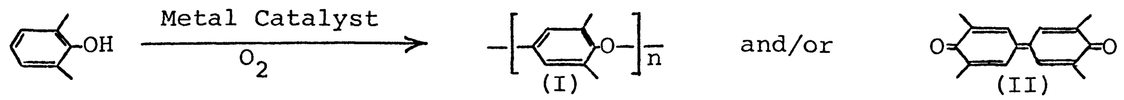
In the oxidation of other phenol derivatives, the catalytic activity of oligo-(NPCA)-copper complex is generally satisfactory, compared with that of pyridine-copper complex which is a conventional and effective catalyst[1]. In particular, thio-oligomer, oligo(NPTCA),-copper catalyst shows a higher activity. The soft-ligand character of thio-oligomer seems to enchance the metal-coordination, resulting in a higher efficiency for formation of catalytically active complex.

Table II. Oxidation of Several Phenols with Copper Complex[a]

Phenol	Oxidation Time(hr)	Conversion (%)[b]		
		Pyridine-Cu[c]	Oligo(NPCA)-Cu[c]	Oligo(NPTCA)-Cu[d]
	4	24	23	41
	10	-	57	89
	4	41	33	39
	10	-	71	80
	4	33	10	24
	4	14	12	26

(a) Oxidation conditions: Phenol concentration, 0.052 M. Concentration of $CuCl_2$, 0.0011 M. Concentration of ligand unit, 0.0037 M. Under O_2 atmosphere at room temperature. (b) Conversion was calculated from GC analysis. (c) in Benzene-MeOH (65:35, v/v) 10 ml. (d) in Benzene-MeOH-DMSO (64:35:1) 10 ml.

Most striking is that oligo(NPCA)-copper catalyst not only promotes the rate of oxidation, but also controls the course of coupling. As well known[1,2], 2,6-xylenol with usual metal catalyst produces poly(phenyleneoxide) (I) by C-O coupling and diphenoquinone (II) by C-C coupling;



We analyzed the oxidation products of 2,6-xylenol by Gel Permeation Chromatography (Shimadzu-Du Pont 803 apparatus with column constitution of HG-60-40-20, eluted with THF). The results are shown in Figure 1, together with diagram of the reference experiment undertaken with pyridine-copper catalyst. The oxidation by using oligo(NPCA)-copper catalyst gives (I) specifically in the wide range of mole ratio of ligand to copper ion, although oxidation by pyridine-copper catalyst gives mixture of (I) and (II).

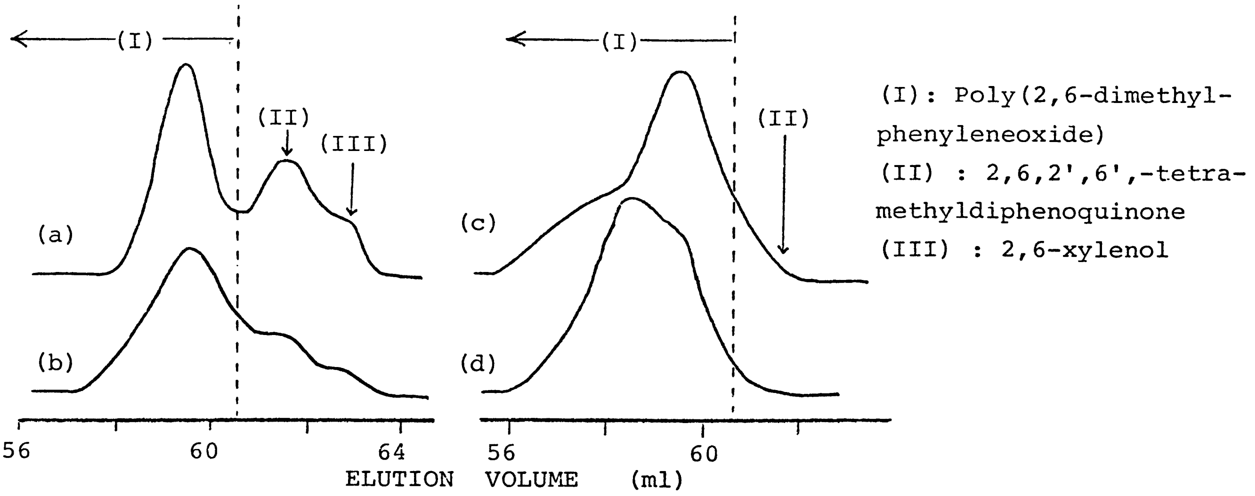


Figure 1. GPC Diagrams of Oxidation Products of 2,6-Xylenol

(a) Products with pyridine-copper complex(pyridine:Cu=4:1). (b) Products with oligo(NPCA)-copper complex(>NCONHPh:Cu=1.1:1.0). (c) Products with oligo(NPCA)-copper complex(>NCONHPh:Cu=4:1). (d) Products with oligo(NPCA)-copper complex (>NCONHPh:Cu=12:1).

The oligomer catalyst was found to be able to accelerate the rate and to control the coupling course of phenol. Although the origin of coupling selectivity is a still unsolved problem, Tsuchida et al.[8] have indicated that C-O coupling selectivity increases as the coordination of phenol to the metal catalyst becomes stronger in the amine-copper catalyst systems. Previously we have reported that oligo(NPCA) shows strong binding power for a variety of small molecules including phenols. Such binding features may lead to the considerable concentration of phenol in the oligomer domain, followed by effective coordination to the metal catalyst. In other words, oligo(NPCA) has an important role to promote the coordination of phenol to the metal catalyst. Further studies on the detailed mechanism of this system are in progress extensively.

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(Received February 19, 1979)