

Catalytic Properties of Synthetic Linear Oligomer-Copper Complexes in Autoxidation of Phenols

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A new type of copper complex composed of intermediate sized ligands was employed as catalyst in the autoxidation of phenols. Among a series of copper catalysts containing urea and thiourea ligands, intermediate sized oligomer ligand [(3), (5), and (8)]-CuCl₂ complexes showed effective catalytic activities in the oxidative coupling of 2,6-xyleneol. Reaction rates were high and there was excellent coupling selectivity. The catalytic properties were much different both from those of smaller ligand-copper complexes and from those of polymeric ligand-copper complexes, and seemed to be characteristic of the present type of catalysts.

A large number of metal complexes have been employed as catalysts in organic reactions. In particular, the unique and effective catalytic properties of copper complexes have received much attention in oxidation reactions.¹ Studies on copper catalysts, dealing with small² and polymeric ligands,³ have emphasized that ligand structure is an essential catalytic property. Recently a new type of metal complex⁴ containing intermediate sized ligands has been demonstrated to have interesting chemical properties, especially facile redox properties. Although this type of complex could have a wide range of oxidation states of their co-ordinated metal ions, few attempts have been made to utilize them as redox catalysts.

We previously developed a one-step synthesis of intermediate sized oligomers with the structure [CH₂CH₂N(CXNHPh)]_n (X = O or S).⁵ They had a definite molecular weight distribution (*n* = 8), and were prepared semi-quantitatively by ring-opening oligomerization of the corresponding aziridine monomers. These oligomers consist of three functionalized regions: (i) a metal chelating site (>NCXNH) that can coordinate to some transition metal ions, (ii) an aromatic group (Ph) that may produce a hydrophobic microenvironment around the active metal ion, as in some metalloenzymes, and (iii) a polyethylenimine main chain which is essentially flexible and enables its functional groups to act cooperatively. These structural features allow several unique chemical functions,⁶ transportation of copper(II) ion across the hydrophobic membrane and anion-binding *via* 'ligand-copper ion-substrate anion' type of ternary complex formation. The hydrophobic properties and anion-co-ordination character of these oligomeric-copper complexes are expected to display effective catalytic activity.

This paper describes the effects of ligands, especially ligand sizes, on the catalytic activities of the copper complexes. We found that some urea-copper complexes, composed of intermediate sized oligomers, showed high catalytic activities in the oxidation of phenols. Although many kinds of copper catalysts affect this reaction, to our knowledge, the present case is the first example of an effective copper catalyst co-ordinated by intermediate sized oligomer ligands.

Results and Discussion

(1) *Autoxidation of 2,6-Xyleneol Catalysed by Copper Complexes.*—We first examined the copper complex-catalysed autoxidation of 2,6-xyleneol. This reaction is a well known

industrial process producing poly(phenylene oxide) derivatives, and has merit for the study of the catalytic property of the metal complex.^{3b} It proceeds *via* 'substrate anion-copper ion-ligand' type of ternary complex formation, so that the properties of the ligand are clearly reflected both in the reaction rate (catalytic activity) and in the coupling pattern of the resulting product (coupling selectivity). Either C-O or C-C coupling takes place [equation (i)].

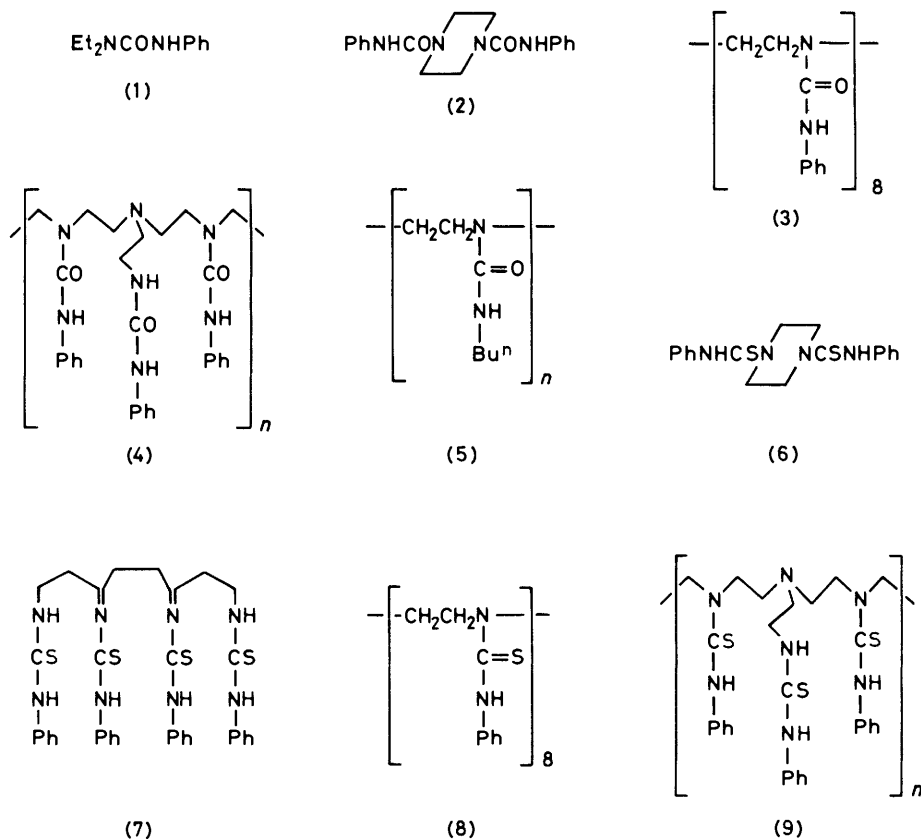
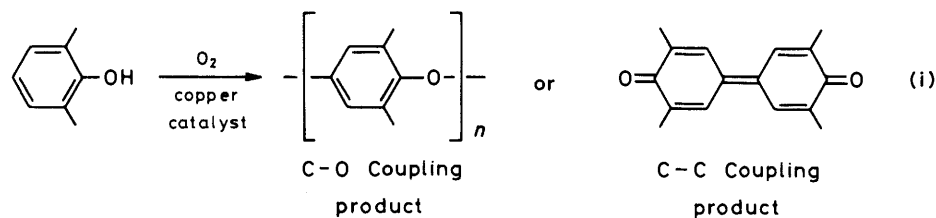
Ligands (1)–(9) were examined. We prepared the octameric ligands [CH₂CH₂N(CXNHPh)]₈ (3; X = O) and (8; X = S) by ring-opening oligomerization of carbamoylaziridine monomers in satisfactory yields.^{5a,c} This oligomerization method, developed by the present authors, is a useful and facile procedure for obtaining linear oligomers of this type. The *n*-butyl group-bearing oligomer (5) was similarly synthesized, but its molecular weight distribution was somewhat broader (*n* = 3–8).^{5b} The ligands (1), (2), (4), (6), (7), and (9) were prepared from corresponding amines and isocyanates for comparison. Most of them, (1)–(6) and (8), formed soluble green copper complexes in methanol-benzene or methanol-benzene-dimethyl sulphoxide.† Exceptionally, two copper complexes involving ligands (7) and (9) were less soluble and were partially suspended in the solvent systems used.

By using these copper complex catalysts, autoxidation of 2,6-xyleneol was carried out under oxygen and typical results are summarized in Table 1.⁷ As the linear relationship between reaction time and conversion was confirmed (conversion < 50%), the conversions indicated in Table 1 can be used as a measure of oxidation rate under the given conditions.

Although many kinds of copper complexes containing amine- or carboxylic acid-type ligands^{2,3} are known to be useful catalysts, we found that some urea- or thiourea-copper complexes are effective in this reaction.

Among a series of copper catalysts, octameric ligand (3) and (8)-CuCl₂ catalysts exhibited significantly better catalytic properties both than the smaller ligand (1), (2), (6), and (7)-CuCl₂ complexes and than the higher molecular weight analogue (4) and (9)-CuCl₂ complexes. The copper complex of *n*-butyl-bearing oligomer (5), which was not composed of pure octamer, also had good activity. These results show that intermediate sized ligand-CuCl₂ complexes are potential catalysts, and also suggest that recurrence of >NCXNHPh groups in a

† No marked change in the electronic spectra of the ligand (1)-CuCl₂ system was observed.



ligand molecule provides high catalytic activities. Siegel *et al.* have examined the catalytic activities of various oligoethylenimine (ene, diene, triene, tetraene, . . .)-copper complexes in the decomposition of hydroperoxide,⁸ and found that smaller ligand-copper complexes are more effective than higher analogues. Hence, the size and shape of the ligands are important but complex factors in determining the properties of the catalysts.

The sulphur-containing octameric ligand (8)-CuCl₂ complex showed higher activity, compared with the corresponding urea ligand (3)-CuCl₂ and conventional pyridine-CuCl₂ systems.^{2a,3b} The introduction of a sulphur atom into the ligand molecule led to stronger chelation to the copper ion, resulting in the formation of the catalytically active complex.

The present intermediate sized oligomer-CuCl₂ catalysts have excellent coupling selectivity in the resulting products [see equation (i)]. When conventional copper catalysts such as the pyridine-CuCl₂ complex were employed in this reaction, a mixture of poly(phenylene oxide) (C-O coupling product) and diphenylquinone derivatives (C-C coupling product) was obtained. In marked contrast, the catalysts (3)- and (8)-CuCl₂ controlled the radical coupling pattern, and gave exclusively poly(phenylene oxide) derivative over a wide range of catalyst compositions. Several ligand modifications have already been tried to control the radical coupling process,³ but the utiliz-

ation of intermediate sized ligand was found to give the higher coupling selectivity.

To determine the nature of the catalyst, the catalytic activity of (3)-CuCl₂ was plotted as a function of molar ratio $[\text{NCONHPh in (3)}]/[\text{Cu}^{2+}]$ (Figure 1). For comparison, the variation of the *d-d* transition absorbance of the copper complex is also illustrated. From the observed maximum in the catalytic activity plot, the molar ratio $[\text{NCONHPh in (3)}]/[\text{Cu}^{2+}]$ of the most catalytically active species could be determined as 4, corresponding to a break at the same ratio in the absorbance plot. By means of laser Raman, far i.r., c.d., and other spectroscopic techniques,^{5a,6a,*} we have confirmed that (3)-CuCl₂ involves co-ordination of four carbonyl groups in an essentially 'square-planar' fashion. Its preliminary cyclic voltammogram showed only three reversible waves, in contrast to that of polymer complex. Therefore, the catalytically active complex is believed to have a uniform structure and excellent stability in the electrochemical sense.

(2) Redox Cycle of Copper Catalyst in the Oxidative Coup-

* When the optically active octameric ligand $[\text{CH}_2\text{C}^*\text{H}(\text{CH}_3)\text{N}(\text{CONHPh})_8]$ was employed as ligand, a typical copper band with diffuse fine structure was observed in its c.d. spectrum. It corresponded to an essentially square-planar configuration.

Table 1. Copper complex catalysed oxidation of 2,6-xylenol

Run	Catalyst	Condition ^a	Time (h)	Yield (%)	C-O Coupling ^b selectivity (%)
1	None	B	4	1	
2	CuCl ₂	B	4	3	
3	Pyridine-CuCl ₂	A	4	23	81
4		A + H ₂ O ^c	4	12	
5	(1)-CuCl ₂	B	20	5	
6	(2)-CuCl ₂	B	20	18	
7	(3)-CuCl ₂	B	4	12	
8		A	4	23	>97
9		A	20	84	>97
10		A + Cuproin ^d	20	14	
11		A + N ₂ ^e	20	2	
12		A + H ₂ O ^c	4	23	
13	(3)-CuCl	A	20	80	97
14	(4)-CuCl ₂	B	4	0	
15	(5)-CuCl ₂	B	10	38	90
16	(6)-CuCl ₂	B	10	7	
17	(7)-CuCl ₂	B	10	7	
18	(8)-CuCl ₂	B	3	35	
19		B	10	94	>96
20	(9)-CuCl ₂	B	10	4	

^a Oxidation conditions: 2,6-xylenol, 0.052M; CuCl₂, 0.0011M; ligand, 0.0044 unit M. O₂ atmosphere at room temperature. Solvent system: (A) benzene-MeOH (65 : 35, v/v) 10 ml; (B) benzene-MeOH-DMSO (64 : 35 : 1, v/v) 10 ml. ^b Determined by means of g.p.c. ^c H₂O (500 equiv. over CuCl₂) was added to the system. ^d Cuproine (8 equiv. over CuCl₂) was added to the system. ^e Under N₂, the oxidation experiment was performed.

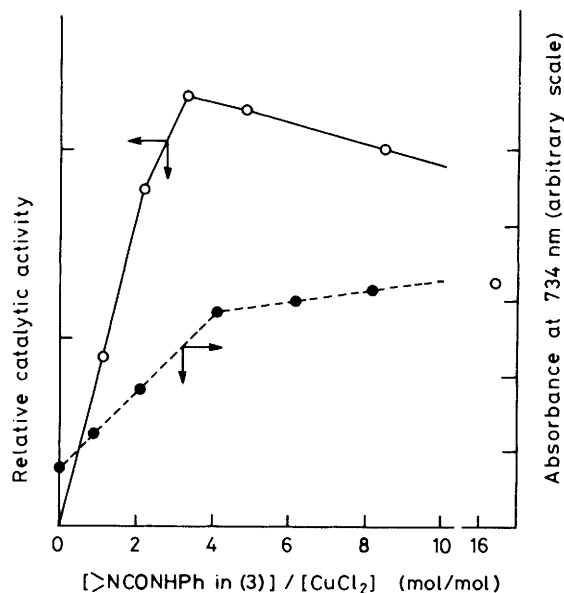


Figure 1. Plot of catalytic activity *versus* catalyst composition. O, Catalytic activity *versus* molar ratio $[\text{NCONHPh in (3)}]/[\text{CuCl}_2]$. Conditions, same as those of Table 1, $[\text{NCONHPh in (3)}]$ was variable. ●, *d-d* Transition absorbance *versus* molar ratio $[\text{NCONHPh in (3)}]/[\text{CuCl}_2]$. Conditions, CuCl₂, 2.5×10^{-4} M in benzene-MeOH (3.5 : 0.5) 4 ml

ling of 2,6-Xylenol.—The reaction profile of the (3)-CuCl₂-catalysed autoxidation of 2,6-xylenol is illustrated in the Scheme:* step 1, phenol substrate co-ordinates to copper(II) catalyst; step 2, one electron transfers from phenol to copper(II) catalyst; step 3, activated phenol substrates couple with each

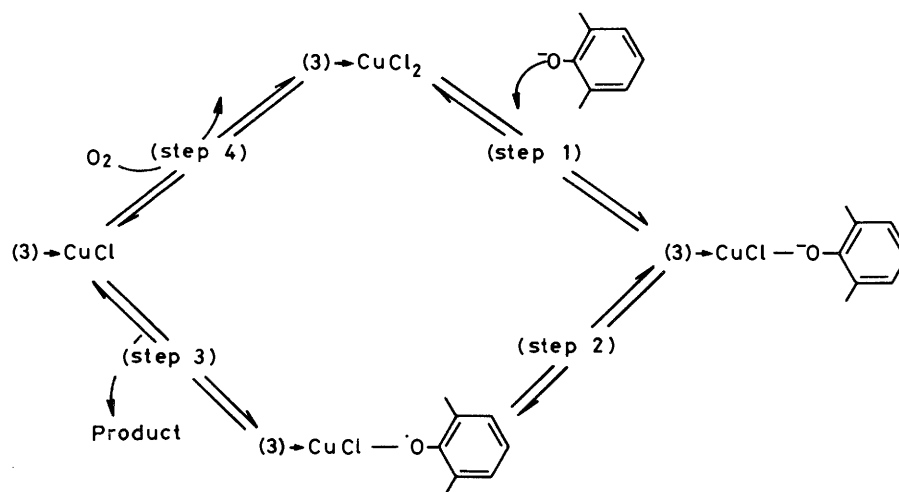
other; step 4, the reduced copper(I) catalyst is oxidized to the original copper(II) catalyst by molecular oxygen.

When 2,6-xylenol was added to (3)-CuCl₂ in solution, a new band appeared at 414 nm (Figure 2). Since this band disappeared on adding a stronger chelating reagent such as salicylic acid, it could be assigned to the band due to the co-ordinated phenoxide anion as a transient species.† It has already been demonstrated that the lipophilic (3)- and (8)-CuCl₂ complexes allowed effective extraction of *p*-nitrophenolate and other inactive phenolate anions from aqueous alkaline solution into methylene chloride solution *via* the 'ligand-copper ion-phenolate anion' type of ternary complex.⁹ This anion-binding property of intermediate sized ligand-copper complexes was clearly observed in the present oxidation. Similar but slight spectroscopic changes were found in the other systems with urea ligands [(1), (2), and (4)], indicating that their complexes could not effectively bind phenolate anions. From Table 2, the absorbance of 2,6-dimethylphenolate anion co-ordinated to the (3)-CuCl₂ complex increased at higher molar ratios of $[\text{NCONHPh in (3)}]/[\text{Cu}^{2+}]$ and showed a maximum at a molar ratio of 4. This composition of the complex corresponds to the catalytically most active species (see Figure 1). On the other hand, the absorbance of the *d-d* transition band of the original copper(II) complex at 734 nm gradually decreased and finally disappeared in the absence of oxygen.

These observations clearly indicate that co-ordination of 2,6-xylenol to the copper catalyst (step 1) and the subsequent electron transfer process (step 2) actually operate in this reaction. Another experiment (Table 1, run 10) shows that oxidation was suppressed by adding cuproine. Since this is a selective and strong chelating reagent for copper(I) ion,¹⁰ the transient copper(I) species, produced in the course of reaction (step 2), could be trapped by cuproine. Therefore, the redox cycle,

* A similar mechanism has already been reported (see ref. 3b).

† The oxidation product (diphenoquinone) may be formed, but we found little trace of it in this system.



Scheme. Mechanism of oxidation of 2,6-xyleneol catalysed by (3)-CuCl₂ complex

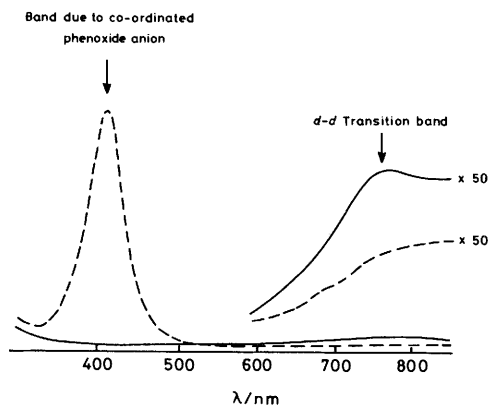


Figure 2. Electronic spectra of (3)-CuCl₂ (—) {[>NCONHPh in (3)]/[CuCl₂] 3.6/1} and (3)-CuCl₂-2,6-xyleneol (---) {[>NCONHPh in (3)]/[CuCl₂]/[2,6-xyleneol] 3.6/1/5.0}. The spectra were recorded immediately after adding 2,6-xyleneol to the catalyst solution under N₂ (ca. 3 min)

oligomer ligand-CuCl₂ ⇌ oligomer ligand-CuCl, plays an important role in this reaction.

Of significance in relation to some enzymatic reactions and in contrast to other copper complex-catalysed reactions,¹¹ this catalyst is capable of oxidizing phenol substrate in the absence of oxygen (Table 1, run 11). Thus molecular oxygen oxidizes copper(I) species only (step 4).

The oligomer ligand (3) showed another important feature in this oxidation: the protection of the catalytically active site from water produced in the reaction. A conventional pyridine-CuCl₂ catalyst was seriously deactivated by adding excess water (500 mol equiv.) to the system. Its catalytic activity was reduced to one-half of the original value under these conditions (Table 1, run 4). On the other hand, (3)-CuCl₂ retained high catalytic activity even in the presence of water (Table 1, run 12). This indicates that the catalytically active copper site was stabilized and protected by the co-ordinated hydrophobic ligand molecule. Although similar observations have been reported for polymer catalysts,³ ligand (3) was large enough to provide a proper hydrophobic domain around the active site of the copper complex.

(3) Effects of Intermediate Sized Oligomer Ligand on Catalytic Properties.—The intermediate sized copper com-

Table 2. Spectral changes of co-ordinated phenoxide anions in the presence of urea-containing ligand-CuCl₂ systems

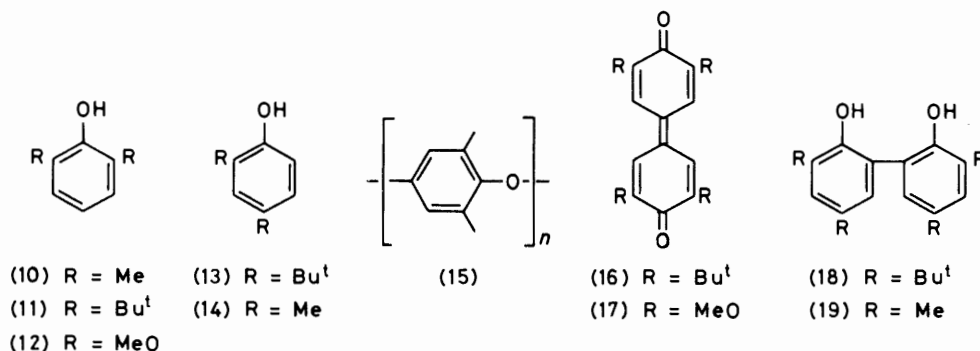
Copper complex	Relative absorbance ^a		
	2,6-Me ₂ -C ₆ H ₃ O ⁻	2,6-Bu ^t ₂ -C ₆ H ₃ O ⁻	2,6-(MeO) ₂ -C ₆ H ₃ O ⁻
CuCl ₂	1.00	1.00	1.00
(1)-CuCl ₂ (4.0 : 1.0) ^b	1.00	1.00	1.00
(2)-CuCl ₂ (4.0 : 1.0)	4.53	2.03	2.28
(3)-CuCl ₂ (1.2 : 1.0)	16.5		
(2.3 : 1.0)	24.0		
(3.6 : 1.0)	36.2	2.32	2.56
(5.8 : 1.0)	40.3		
(4)-CuCl ₂ (4.0 : 1.0) ^d	8.42	2.41	2.33
λ _{max} /nm	414	418	461 ^c

^a Each value was standardized from that in the case of CuCl₂ alone. Conditions; CuCl₂, 0.0025M; phenol, 0.0125M; solvent, MeOH-benzene (7 : 3, v/v) 4 ml. ^b Values in parentheses indicate molar ratio [>NCONH unit]/[CuCl₂]. ^c Partial reaction occurred in this system. ^d Solvent system, MeOH-benzene-DMSO (7 : 2.5 : 0.5) 4 ml.

plexes (3), (5), and (8) have largely different properties from the smaller and polymeric ligand-copper complex catalysts. This can be called an 'oligomer effect'^{7b,c} in the same sense as the 'polymer effect',³ and explained by considering, at least, two factors: (i) effective formation of a catalytically active copper complex; (ii) facile substrate co-ordination to the copper complex, followed by an electron transfer reaction.

The stability constants of copper complexes for several urea ligands were determined from the variation of *d-d* transition absorbance plots as follows: (1) (very small) < (2) (710) < (3) (2 270) < (8) (3 340) > (4) (225 l mol⁻¹). This trend parallels that of the catalytic activities as shown in Table 1, and denotes that a number of neighbouring >NCX-NHPh groups in a single ligand molecule are required to form a catalytically active complex. Unexpectedly, polymeric ligand (4) appeared to be unfavourable for complexation because of its size.

As suggested by Tümmeler *et al.*,^{4e} the flexible nature of linear oligomer ligand has advantages for dynamic conformational changes. The redox reaction, Cu²⁺ ⇌ Cu⁺, requires rearrangement of the copper complex, but linear oligomer



ligands may easily undergo expansion and contraction in the electron transfer and reoxidation processes (steps 2 and 4 in the Scheme).

The intermediate sized ligand-CuCl₂ catalysts seem to result in not only higher reaction rates but also excellent radical coupling selectivities in the resulting products. Although the detailed mechanism still remains unclear, the high coupling selectivity may be caused by polarization of the co-ordinated phenol substrate which is determined by the complex structure. Kinetic studies by Tsuchida *et al.*¹² have led to the conclusion that greater formation constants of the 'substrate-copper ion-ligand' complex lead to higher C-O coupling selectivity. This conclusion is supported by our results that intermediate sized ligand-copper catalysts promote the formation of a transient ternary complex and a highly controlled radical coupling pattern. As proposed for related systems,¹² the phenoxide radical may attack a polarized *para*-carbon atom in another co-ordinated phenol substrate in the co-ordination sphere of the copper catalyst.

(4) *Application of Oligomer-Copper Catalyst to Oxidation of Other Phenols.*—Our copper catalysts were applied to the oxidation of 2,6-dimethoxyphenol, 2,6-di-*t*-butylphenol, 2,4-di-*t*-butylphenol, and 2,4-xyleneol. The oxidation rates were slightly accelerated, compared with that of 2,6-xyleneol (Table 3).

As shown in Table 2, co-ordination of these substrates to the copper complex was slightly promoted in the presence of oligomer ligand (3). Although these substrates are more susceptible to oxidation, bulky substituents such as *t*-butyl and methoxy may hinder access of the substrates to the active copper ion. A similar steric effect on the formation of the 'substrate-copper ion-ligand' type of ternary complex has been reported for a related system. These results suggest that substrate co-ordination (step 1 in the Scheme) is a critical factor in determining the activity of the present catalyst system.

We have presented a significant example of a new type of catalyst. The catalytic activity of copper complexes in the autoxidation of phenols is increased by using intermediate sized oligomer ligands. These catalysts have several advantages over related smaller and polymeric catalysts. (i) They act as a strong metal chelating reagent due to the effective co-operation of binding sites in a single chain. (ii) The ligand molecule has a spatial arrangement favourable for substrate co-ordination to copper ion. (iii) Protection of the active site by the hydrophobic microenvironment of the ligand can be expected. (iv) The higher mobility of this type of complex is also effective.

Experimental

Ligand Synthesis.—Octameric oligo[1-(*N*-phenylthiocarbamoyl)aziridine] (3) was prepared by ring-opening oligomeriz-

Table 3. Copper complex catalysed oxidation of phenols^a

Phenol	Time (h)	Conversion (%)			Main product
		Pyridine-CuCl ₂ ^b	(3)-CuCl ₂ ^b	(8)-CuCl ₂ ^c	
(10)	4	23	23	47	(15)
	20		84		
(11)	4	24	23	41	(16)
	20		80		
(12)	4	41	33	39	(17)
	20		91		
(13)	4	14	12	26	(18) ^d
(14)	4	33	10	24	(19) ^d

^a Oxidation conditions: phenol, 0.052M; CuCl₂, 0.0011M; ligand, 0.0044 unit M. Under O₂ at room temperature. ^b In benzene-MeOH (65:35, v/v) 10 ml. ^c In benzene-MeOH-DMSO (64:35:1) 10 ml. ^d Structures identified by comparison with the samples provided by Professor I. Tanimoto, Kyoto Women's College.

ation of 1-(*N*-phenylthiocarbamoyl)aziridine with diethyl sulphate.^{5a} Aziridine monomer (0.0020 mol) and diethyl sulphate (0.0020 mol) were dissolved in dry ethyl acetate (10 ml) under argon at room temperature, and the mixture was then allowed to stand at 60 °C for three weeks. The deposited product was separated by removing ethyl acetate and was then washed with ethyl acetate several times. The resulting product was reprecipitated from THF solution by adding ether. After the crude oligomer powder was immersed in a 10% aqueous ammonia solution at room temperature overnight, it was dissolved in THF, and the solution was eluted through an Amberlite 400 column, evaporated, and dried *in vacuo* (yield 40–60%).

Octameric oligo[1-(*N*-phenylthiocarbamoyl)aziridine] (8) and oligo[1-(*N*-*n*-butylthiocarbamoyl)aziridine] (5) were similarly obtained, and purified as described before.^{5b,c} The yield of (8) was 80% and of (5) 60%.

G.p.c. analysis indicated that (3) and (8) were octamers but (5) was a mixture of oligomers whose degrees of polymerization were 3–8.

The polymeric thiourea-containing ligand (9) was synthesized from commercial polyethylenimine (Nihon Shokubai Chem. Ltd.; mol. wt. 30 000–100 000) and phenyl isothiocyanate. The original polyethylenimine contained tertiary and secondary nitrogen atoms in the ratio of 1:2. To dehydrated polyethylenimine (2.15 g) suspended in dried benzene (50 ml), phenyl isothiocyanate (11.0 g) was added dropwise with vigorous stirring. After additional stirring for 6 h, benzene was removed under reduced pressure. The residue was washed with ethanol in a Soxhlet extractor for 10 h. The ¹H n.m.r. spectrum of this product showed that more than

85% of the secondary and primary nitrogen atoms in the original polyethylenimine had reacted (yield 75%).

The other ligands were obtained from the corresponding amines and isocyanates in good yields: (1), 95%; (2), 90%; (4), 70%; (6), 80%; (7), 40%. The detailed procedures and significant spectral data have been reported previously.^{5b,d,6a}

Oxidation Procedure.—The catalysts were obtained by mixing CuCl₂ and the ligand molecules *in situ*, and were used without further purifications. The oxidation of phenols was generally performed in a 30 ml reactor connected to a 100 ml gas burette. The stirred reaction solution containing copper catalyst and phenol substrate was subjected to oxygen at a pressure of 1 atm. at ambient temperature (ca. 20 °C). The catalysts were dissolved in the reaction solution during the oxidation reaction, except for ligand (7)– and (9)–copper complexes. The conversion rates of the oxidation were determined by means of gas and liquid chromatography. It was also possible to follow the progress of the reaction by the changes of volume in the gas burette.

Oxidation Products.—The products were identified by comparison with authentic samples prepared according to the literature methods: poly-(2,6-dimethylphenylene oxide),^{13a} yield 80%; 2,6-dimethyl-*p*-benzoquinone,^{13b} 50%; 2,2',6,6'-tetramethyldiphenylquinone,^{13b} 50%; 2,2',6,6'-tetramethoxydiphenylquinone,^{13c} 70%; 2,2',6,6'-tetra-*t*-butyl-diphenylquinone,^{17d} 95%. The C–O coupling selectivity of the product in the oxidation of 2,6-xyleneol was determined by means of gel permeation chromatography (Schimadzu–Du Pont model 830 apparatus with an SG-60-40-20 column).*

* The molecular weights of the polyphenylene oxides obtained (C–O coupling product) were generally 3 000–10 000.

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