New Catalytic Systems for the Oxidative Polymerization of 2,6-DimethyIphenol

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ABSTRACT

A new principle for improving the catalytic activity of the classical complexes $CuCl_2$-aliphatic amines used for the oxidative coupling of 2,6-dimethylphenol (DMP) is presented. It is based on the "trans" effect, typical of the substitution reactions of ligands in the square planar complexes of platinum(II). Thus, by replacing a Cl^- anion with a strong "trans" effect-giving ligand such as NO_2^-, CN^-, RS^-,

$$SO_3^{2-},\ S_2O_3^{2-},\ \text{and}\ -\!\!\overset{\displaystyle O}{\underset{\displaystyle OCH_3}{\overset{\|}{P}}}\!\!\begin{smallmatrix}OCH_3\\ \\ \end{smallmatrix}$$

, a significant increase in the rate of oxidative coupling of 2,6-DMP is observed. It was quantitatively estimated by measuring the oxygen absorption rate. The highest reaction rates are given by complexes having Cu–S bonds (mercaptides, thiophenolates, thiosulfates). These bonds, which probably have a high oxygen affinity, are typical for copper-containing enzymes (laccase, tyrosinase, ascorbic acid oxidase), redox enzymes that catalyze the oxidative coupling of some natural phenols very efficiently.

INTRODUCTION

Soon after Allan S. Hay (General Electric Research Laboratories) reported in 1959 the oxidative polymerization of 2,6-disubstituted phenols to yield high molecular weight polyphenylene oxides, a representative of this class, poly(2,6-dimethyl-1,4-phenylene oxide) became one of the most important engineering polymers due to its high performance properties. The reaction occurs in mild conditions (room temperature, atmospheric pressure) in the presence of Cu^{2+}-amine catalytic complexes:
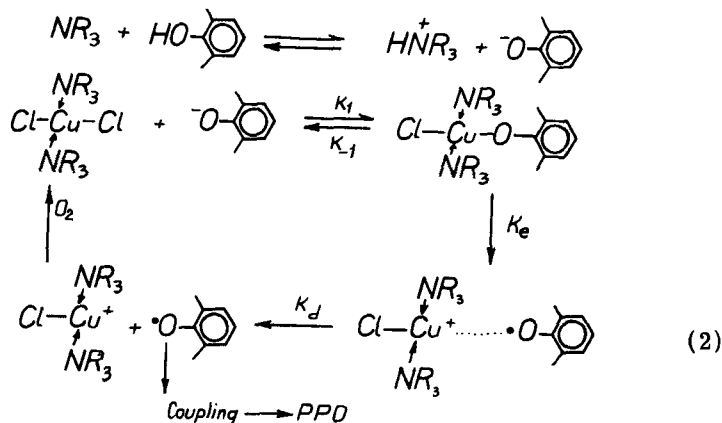

$$\tag{1}$$
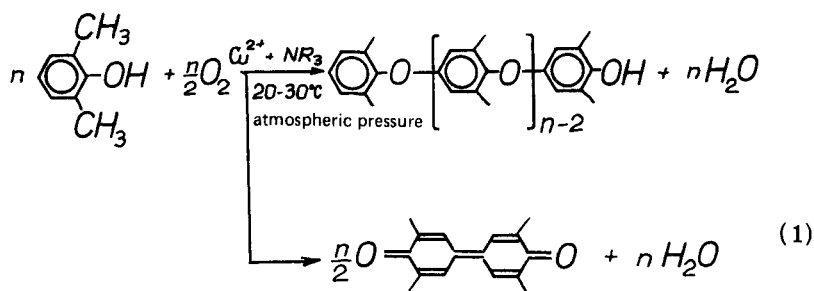
The high yield of the reaction, the high oxygen consumption rates, the unexpected mild reaction conditions, and the kinetic scheme, similar to that of Michaelis–Menten and characteristic of enzymatic reactions, are evidence of the astonishing resemblance with several natural redox processes (including the oxidative coupling of natural phenols) catalyzed by Cu-enzymes (laccase, tyrosinaze, ascorbic acid oxidaze, plastocyanine), real activators of molecular oxygen, which play a decisive role in the processes governing the living world. There is no doubt but that there is a catalytically active center which is where copper is complexed by the protein by specific ligands. Thus, CN^- anions completely inhibit the catalytic activity.

Among known catalytic systems are CuCl-Py [1, 2], $CuCl_2(CuBr_2)$-di-n-butylamine [3], $CuCl_2$-morpholine [4], CuCl-tetramethylethylene diamine [2], $Cu(HCOO)_2$-Py [5], and Mn(ll)-benzoinoxime [6].

Studies concerning the action mechanism of these catalysts give evidence that the real oxidizing agent is Cu^{2+}, which by a "one electron transfer" is reduced by the xylenolate anion (which turns to an aryloxy radical) to Cu^+, oxygen being responsible for the reoxidation of Cu^+ to Cu^{2+} [2, 7].

Reaction (2) is, in fact, a bimolecular nucleophilic substitution, the Cl^- anion being substituted for by the xylenolate anion. Kresta and co-workers [8] demonstrated that the active catalytic complex in the

$$NR_3 + HO\text{-}\bigcirc \rightleftharpoons H\overset{+}{N}R_3 + {}^-O\text{-}\bigcirc$$

$$\begin{array}{c} NR_3 \\ | \\ Cl\text{-}\overset{|}{C}u\text{-}Cl \\ | \\ NR_3 \end{array} + {}^-O\text{-}\bigcirc \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \begin{array}{c} NR_3 \\ | \\ Cl\text{-}\overset{|}{C}u\text{-}O\text{-}\bigcirc \\ | \\ NR_3 \end{array}$$

$$\downarrow O_2 \qquad\qquad\qquad \downarrow K_e$$

$$\begin{array}{c} NR_3 \\ | \\ Cl\text{-}\overset{|}{C}u^+ \\ | \\ NR_3 \end{array} + {}^\bullet O\text{-}\bigcirc \overset{K_d}{\longleftarrow} \begin{array}{c} NR_3 \\ | \\ Cl\text{-}\overset{|}{C}u^+ \cdots\cdots {}^\bullet O\text{-}\bigcirc \\ | \\ NR_3 \end{array} \qquad (2)$$

$$\downarrow$$
$$Coupling \longrightarrow PPO$$

oxidative polymerization of 2,6-xylenol is square planar, paramagnetically active.

It is known that chemical reactivity of complex combinations is strongly dependent on the ligands situated in the coordination sphere of the metal, the influence of these ligands being transmitted to the other ligands by means of the central metal ion. Such effects have been clearly evidenced for the complex combinations of Pt(II) which has a square planar configuration [9]. The phenomenon, known as the "trans" effect, only appears when a ligand produces a significant weakening effect on a trans bond, much more than on a cis bond.

The ligands having a strong "trans" activity in the case of square planar complexes of Pt(II) are $X = CN^-$, NO_2^-, $S_2O_3^{2-}$, SCN^-, PR_3,

$R_2S > I^- > Br^- > Cl^- > NR_3 > OH$:

$$\begin{array}{c} Cl \qquad Cl \\ \diagdown \quad / \\ Pt \\ / \quad \diagdown \\ X \qquad Cl \end{array}$$
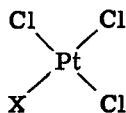
$$I$$

The Cl^- anion situated trans with respect to X is markedly weakened due to the polarization effects transmitted by means of the central metal ion, thus increasing its reactivity in the substitution reactions.

The substitution reactions of type I complexes occur mainly by replacing the Cl^- anion situated trans, the "cis" ligands being much more difficult to substitute, and sometimes only under drastic conditions:
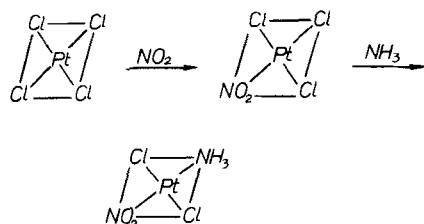
Similar to the square planar Pt(II) complexes, increasing the catalytic activity of the $CuCl_2$-morpholine complex was attempted by substituting a Cl anion with a trans active ligand.

EXPERIMENTAL

Materials

2,6-DMP was purified by recrystallization from n-hexane. Toluene was dried on molecular sieves. Morpholine and tetramethylethylenediamine were used after being dried over potassium hydroxide. $CuCl_2$, NaBr, $NaNO_2$, Na_2SO_3, $Na_2S_2O_3$, and NaCN were used as ~2% solutions in methanol. Dimethylphosphite, hydrazine, phenylhydrazine, and tert-dodecylmercaptan were also used as 2 g/100 mL solutions in methanol.

Polymerization Tests

In order to evaluate the effect produced by introducing trans active ligands in the classic $CuCl_2$-morpholine complex, two kinds of experiments were performed: (a) reaction exotherm determination; (b) oxygen absorption kinetics.

Thus, in methanol, the $CuCl_2$-morpholine complex was modified by reacting it with NaBr, $NaNO_2$, $Na_2S_2O_3$, Na_2SO_3, ⟨O⟩—SH , hydrazine, phenylhydrazine, and tert-dodecylmercaptan. The $CuCl_2$-morpholine catalytic complex was taken as the standard for both tests.

(a) Reaction Exotherm

As in any oxidation reaction, polymerization by oxidative coupling of 2,6-DMP is an exothermic reaction, heat resulting mainly from molecular oxygen turning into water.
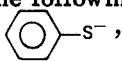
The tests were performed in a three-necked reaction vessel, magnetically stirred, equipped with a thermometer and a reflux condenser, and thermally isolated.

The temperature increase was plotted against time for the standard complex and for modified complexes.

(b) Oxygen Absorption Kinetics

Oxygen consumption rates for different catalytic systems, tested by the oxidative polymerization of 2,6-DMP, were carried out in a classic system consisting of a magnetically stirred reaction vessel attached to a gas burette. Oxygen consumption was plotted against time.

RESULTS AND DISCUSSION

By following the temperature rise against time (Fig. 1), the relativity of the catalytic activities of Cu^{2+}-amine complexes, modified with different "trans" active ligands, can be evaluated. The following ligands were employed: SO_3^{2-}, $S_2O_3^{2-}$, S^{2-}, Br^-, NO_2^-, ⟨O⟩—S^-, RS^-, and CN^-.

By analyzing the curves it is concluded that all the "trans" active ligands mentioned lead to higher values of the temperature rise rates and to higher values of the maximum temperature (t_{max}) than those obtained with the classical complex.

The ligands leading to Cu–S bond formation proved to be the most efficient "trans" active ligands (mercaptides, thiophenolates, thiosulfate).

In Fig. 2 the kinetic curves of oxygen consumption are given for the complexes mentioned above.

The following relative order has been established:

$$RS^- > {}^-S-⟨O⟩ > S^{2-} > S_2O_3^{2-} > Br^- > NO_2^- > CN^-.$$
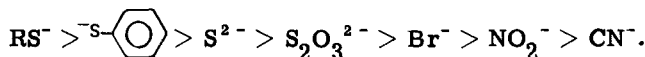
In Table 1 the following data are presented: t_{max}, slurry appearance time, relative viscosity, and yield of the polymers resulting from the modified catalytic complexes compared with the standard complexes.

In Fig. 3 the effects of the "trans" active ligands on polymer yield are presented. These ligands lead to higher yields than the standard catalytic complex.

It is observed that the relative order of the catalytic activity is somewhat different from the relative order of the "trans" activity of square planar Pt(II) complexes. Probably the new ligands effect not only the rate of Cl^--xylenolate interchange, but also the rates of "one electron transfer" (k_e), dissociation of the activated complex (k_d), and the oxygen affinity of the catalytic complex.
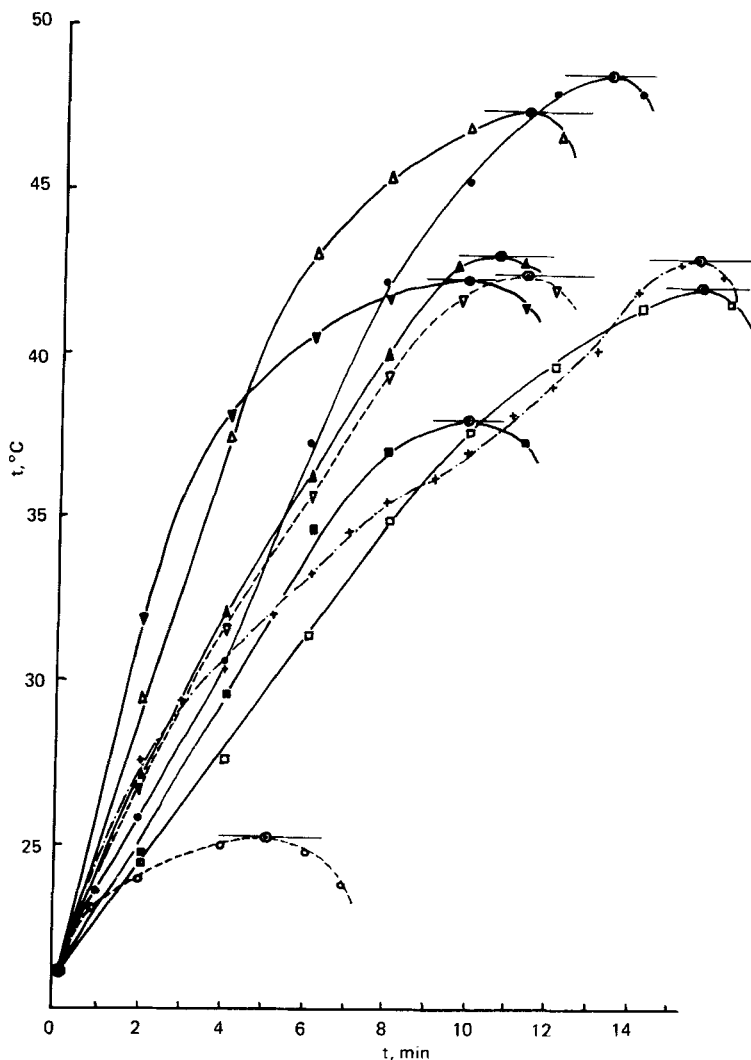
FIG. 1. Temperature rise against time for the oxidative polymer-
ization of 2,6-dimethylphenol in the presence of "trans" active agents.
($\bullet$) $CuCl_2$-Na_2SO_3-morpholine, ($\triangle$) $CuCl_2$-tert-dodecylmercaptan-
morpholine, ($\blacktriangle$) $CuCl_2$-$NaNO_2$-morpholine, ($\triangledown$) $CuCl_2$-dimethylphos-
phite-morpholine, ($\blacktriangledown$) $CuCl_2$-thiophenol-morpholine, (+) $CuCl_2$-Na_2-
S_2O_3-morpholine, ($\square$) $CuCl_2$-NaCN-morpholine, ($\blacksquare$) $CuCl_2$-morpho-
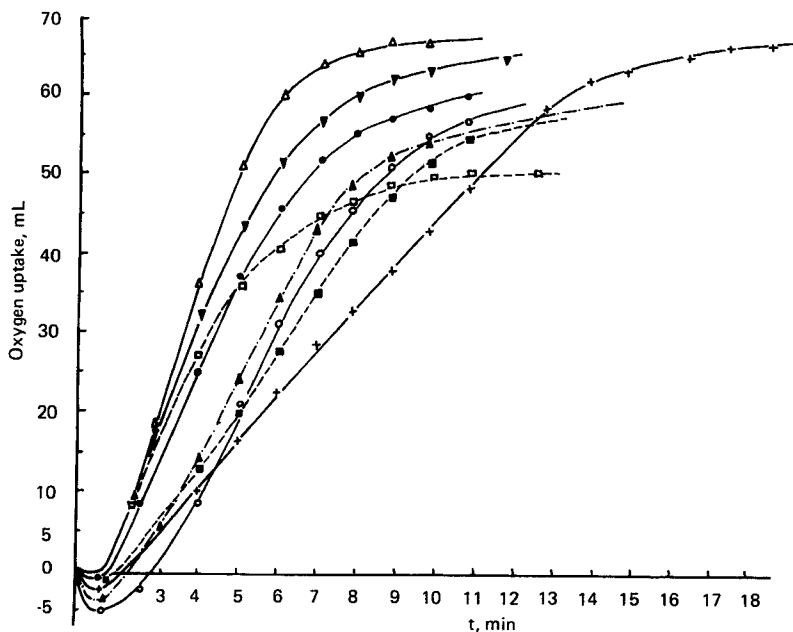line, ($\circ$) CuCl-morpholine.

FIG. 2. Oxygen consumption rate for the oxidative polymerization of 2,6-dimethylphenol in the presence of "trans" active agents. ($\triangle$) $CuCl_2$-tert-dodecylmercaptan morpholine, ($\blacktriangledown$) $CuCl_2$-$Na_2S_2O_3$-morpholine, ($\bullet$) $CuCl_2$-thiophenol-morpholine, ($\circ$) $CuCl_2$-NaCN-morpholine, (+) $CuCl_2$-morpholine, ($\blacktriangle$) $CuCl_2$-dimethylphosphite-morpholine, ($\blacksquare$) $CuCl_2$-$NaNO_2$-morpholine, ($\square$) $CuCl_2$-Na_2SO_3-morpholine.

If chelates are used in which Cl^- anions are situated in the "cis" position (for instance, tetramethylethylenediamine), and Cl^- is substituted by NO_2^- (the NO_2^- group occupies the "cis" position toward Cl^-), the acceleration effect of the reaction is not significant (Fig. 4).
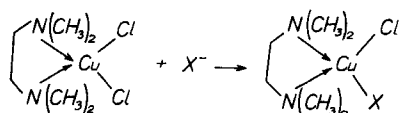
Nonionic compounds have also been used as activating agents. The same evaluation as discussed above has been made for hydrazine and phenylhydrazine. Oxygen consumption and temperature rise were

TABLE 1

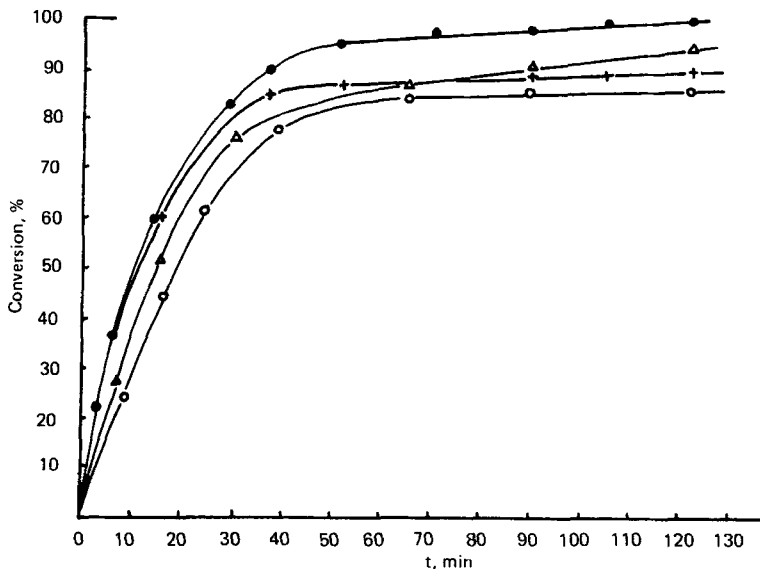| No.	"Trans" active ligand	T_{max}, °C	Slurry appearance time, min	Relative viscosity, dL/g (CHCl$_3$, 30°C)	Polymer yield, %
1	Cl⁻	38	9	0.66	85
2	NO_2^-	43	8	0.60	98
3	$S_2O_3^{2-}$	44.5	15	0.73	84.6
4	Br⁻ / O	47	12	0.94	85.6
5	$P-(OCH_3)_2$	43	10	0.68	80
6	RS⁻	47.5	12	0.75	94
7	SO_3^{2-}	48	14	1.14	80
8		43.5	10	0.473	88
9	S^{2-}	46.5	16	0.727	–

FIG. 3.   The effect of "trans" active agents on polymer yield.
(○) $CuCl_2$-morpholine, (+) $CuCl_2$-thiophenol-morpholine, (△)
$CuCl_2$-tert-dodecylmercaptan morpholine, (●) $CuCl_2$-$NaNO_2$-
morpholine.

plotted against time (Figs. 5 and 6). Both temperature rise, t_{max},
and oxygen consumption rates were found to be higher than those
obtained with the classic complex.

The performance of the CuCl-morpholine complex has also been
tested, as can be seen in Figs. 1 and 5. Its catalytic activity is weak.

The cause of the catalytic activity increase has not been eluci-
dated.

Hydrazine might reduce Cu^{2+} to the lower valency, but the CuCl-
morpholine complex is a very weak catalyst, mainly because of its
low solubility in the reaction medium. Nevertheless, CuCl resulting
"in situ" could be so finely dispersed that it might act as a good
catalyst.

On the other hand, a chelate may result from the reaction between
$CuCl_2$ and hydrazine. In this case the "trans" effect might be re-
sponsible for the catalytic activity increase.

It is not surprising that the highest polymerization rates were
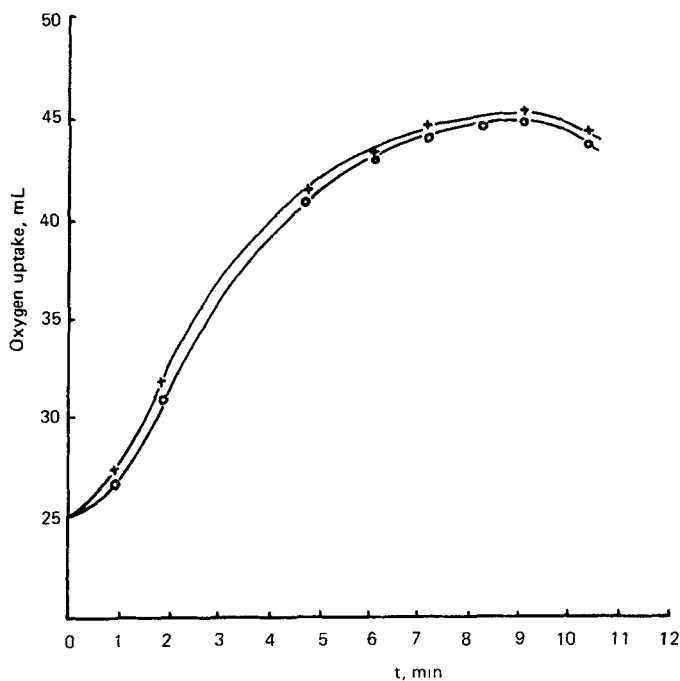obtained in the presence of Cu–S bonds containing ligands.

FIG. 4. Temperature rise against time for the oxidative polymerization of 2,6-dimethylphenol in the presence of $CuCl_2$-tetramethylethylenediamine catalytic complex. (o) $CuCl_2$-tetramethylethylenediamine, (+) $CuCl_2$-$NaNO_2$-tetramethylethylenediamine.

Studies have been made which clearly show that in Cu-containing enzymes the central metal is bonded by the sulfur atom of cysteine or methionine. Kronek and co-workers [12] reported that Cu-S bonds have high oxygen affinity. This bond is responsible for the blue color of those Cu-proteins.

Dooley and co-workers [10], following highly accurate studies, proposed for the active center of lacasse-type enzymes (known to catalyze the oxidative coupling of coniferyl alcohol) the following structure in which Cu is bonded by a S atom of cysteine, two imidazole rings coming from hystidine, and a fourth ligand, X, which may be typical for proteins (for instance, COOH of amino acids).

Laccase contains four Cu atoms/molecule, 0.2-0.46% Cu, and $\overline{M}$ = 60,000-120,000.
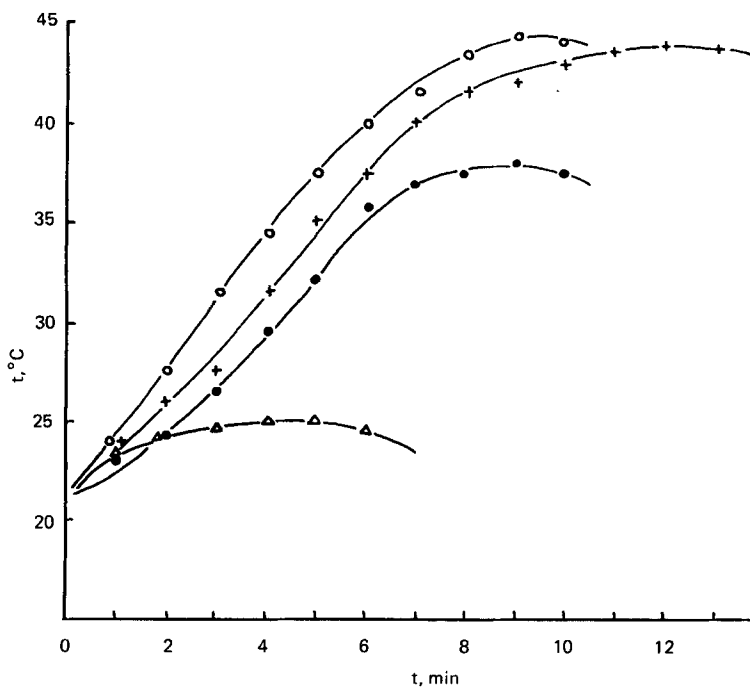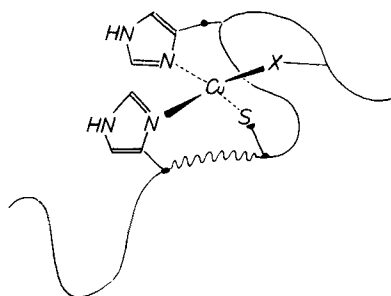
FIG. 5. Temperature rise against time for the oxidative polymerization of 2,6-dimethylphenol in the presence of nonionic activating agents. (o) $CuCl_2$-phenylhydrazine-morpholine, (+) $CuCl_2$-hydrazine-morpholine, (•) $CuCl_2$-morpholine, (△) CuCl-morpholine.

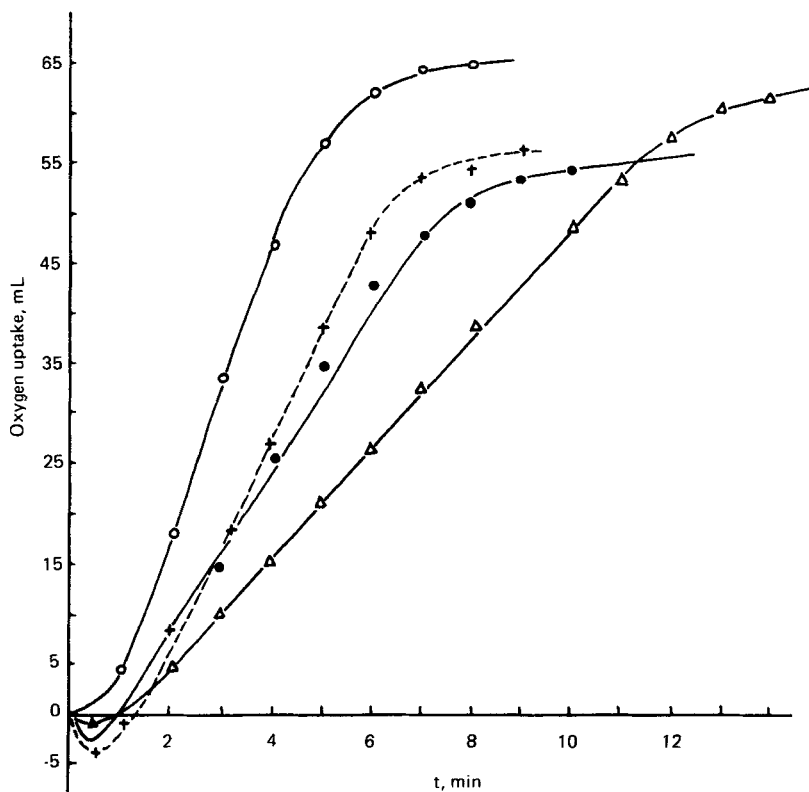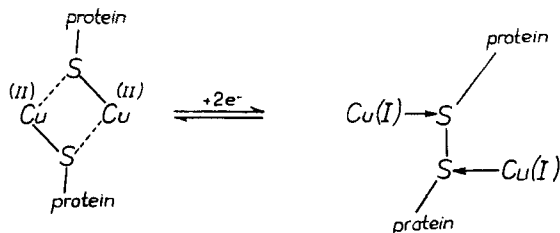For plastocyanine, azurine, and stellacyaninetype enzymes, X of the active center is S, coming from methionine [11].

FIG. 6. Oxygen consumption rate for the oxidative polymerization
of 2,6-dimethylphenol in the presence of nonionic activating agents.
(o) $CuCl_2$-tert dodecylmercaptan-morpholine, (+) $CuCl_2$-phenylhydra-
zine-morpholine, (△) $CuCl_2$-morpholine, (●) $CuCl_2$-hydrazine-mor-
pholine.
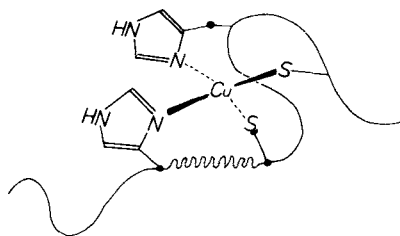
For enzymes containing Cu^{2+} undetectable by ESR, Kronek and co-
workers [12] proposed a model based on the following redox mechanism:

$$2\,Cu(I) + R\text{--}S\text{--}S\text{--}R \rightleftharpoons \underset{\displaystyle \overset{\displaystyle Cu}{(\text{II})}\;\; \overset{\displaystyle Cu}{(\text{II})}}{\overset{\displaystyle \overset{R}{|}\\ S}{\underset{\displaystyle \underset{\displaystyle R}{|}\\ S}{}}} \rightleftharpoons Cu(II) + 2\,RS^-$$
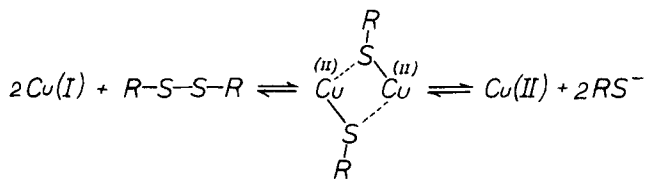
It is very probable that the most active complexes are of the type

$$R\text{--}S\text{--}\underset{\displaystyle \underset{H}{|}\\ N}{\overset{\displaystyle \overset{H}{|}\\ N}{Cu}}\text{--}Cl$$
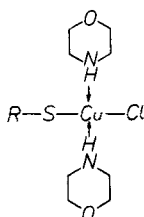
which are similar to the Cu-enzymes complexes.

They may act in the same manner by the same redox mechanism, the electrons being provided by the xylenolate anion which passes through the aryloxy radical state.

CONCLUSIONS

In this paper a new principle for increasing the catalytic activity of Cu^{2+}-aliphatic amines in the oxidative polymerization of 2,6-xylenol has been presented. This principle is based on the introduction of "trans" active ligands in the coordination sphere of Cu^{2+}. All the substituents tested, ⬡—S⁻ , RS^-, $S_2O_3^{2-}$, SO_3^{2-}, Br^-, NO_2^-,

CN^-, and $-\overset{O}{\underset{}{P}}(CH_3)_2$, lead to higher polymerization rates than those obtained by using the standard complex, $CuCl_2$-morpholine.

The highest polymerization rates were obtained using Cu–S bonds containing complexes with high oxygen affinity, very similar to the active center of Cu-enzymes.

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