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Effect of Ligand Ratio on the Catalytic Activity of Poly(4-vinylpyridine)–Copper(II) Chelate in the Oxidation of Thiosalts by Molecular Oxygen

The advantages inherent in attaching homogeneous catalysts to polymers have stimulated extensive research with respect to techniques of achieving such attachment and studies of catalytic activity of the resulting polymer-anchor catalysts. Comprehensive discussions of this field have recently been given (*1*, *2*). Following previous work (*3*) by one of us which showed the ability of copper(II) ammine complexes in aqueous solutions to catalyze the oxidation of thiosulfate to sulfate by molecular oxygen at ambient temperatures, efforts were directed toward developing polymer-supported catalysts having this property as this would facilitate catalyst recovery and reuse, thus providing an inexpensive method for the removal of polythionate contaminants (by complete oxidation) in effluent wastes (*4*). Because of their ability to react strongly with metal ions, chelating polymers have found widespread applications. Copper(II) complexes of one such chelating polymer, namely, poly(4-vinylpyridine) (PVP), have been found to be effective catalysts for the air oxidation of thiosulfate, trithionate, and tetrathionate at ambient temperatures (*5*). An important aspect of polymer-supported catalysis is that the polymer matrix may activate the metal ion by promoting a higher degree of coordinative unsaturation due to limitations in polymer chain mobility, and if the equilibrium within the polymer matrix is shifted toward a lower coordination, the catalyst should be more active (*6*). In view of this hypothesis, it was considered to be of interest to study the effect of the ligand–copper ratio on the activity of PVP–Cu(II) complexes with regard to the above air-oxidation catalysis.

The monomer, 4-vinylpyridine (Polysciences, Inc., Warrington), purified by distilling twice, was polymerized using cumene hydroperoxide (78%) initiator to the extent of 0.6% (w/v), in sealed ampoules, by heating in a water bath at 55°C for 72 h. The resulting polymer (PVP) had an average molecular weight of 3.4×10^5. It was dissolved in absolute methanol to prepare a 2% (w/v) solution. Calculated amounts of the polymer solution and a methanolic solution (2% w/v) of $CuSO_4 \cdot 5H_2O$ were mixed and slowly evaporated to dryness with continuous mixing. The product was washed several times with deionized water, followed by methanol, and then dried in an oven at 50°C under vacuum. The copper content of the complexes was determined by leaching the polymeric catalysts with mineral acid followed by careful addition of concentrated ammonia to fully form $Cu(NH_3)_4^{2+}$ which was analyzed for by visible spectrophotometry at 600 nm with reference to a calibration curve prepared for standard solutions of $Cu(NH_3)_4^{2+}$. A number of copper complexes of PVP having copper content in the range of 3 to 19% (by weight) were thus prepared.

The rate of oxygen consumption for thiosalt oxidation was measured using the constant-pressure gas uptake apparatus and procedure described previously (*7*). The dry catalyst particle diameter in each case

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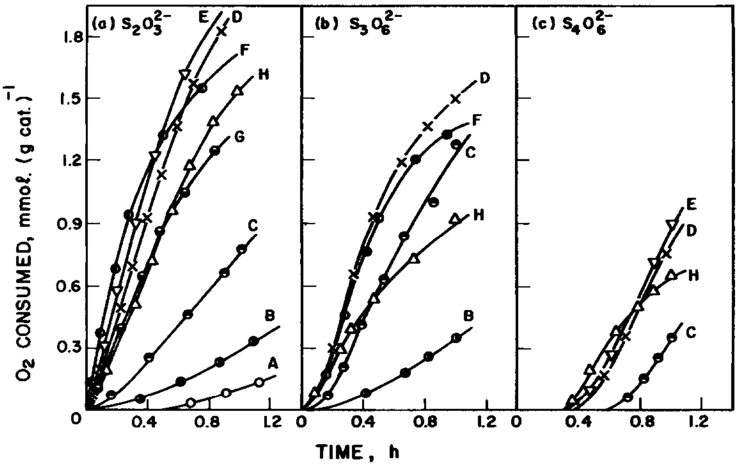

FIG. 1. O_2 consumption versus time at 30°C, 94.0 kPa O_2, and 50.0 mmol liter^{-1} concentration of polythionate: (a) $S_2O_3^{2-}$; (b) $S_3O_6^{2-}$; and (c) $S_4O_6^{2-}$ in the presence of poly(4-vinylpyridine)-Cu(II) complexes of different copper contents: (A) 3.05%; (B) 5.60%; (C) 9.03%; (D) 11.32%; (E) 12.09%; (F) 13.61%; (G) 15.05%; and (H) 18.57% (by weight).

was less than 38 μm in size. The results are plotted in Fig. 1. The initial rates, defined as the maximum rate in the O_2 consumption following the initial curved region, have been measured from the slopes of the curves in Fig. 1 and are plotted in Fig. 2 as a function of copper content or ligand ratio, defined as [pyridine units in PVP]$_t$/[Cu]$_t$. The curves for the oxidation of $S_2O_3^{2-}$, $S_3O_6^{2-}$, and $S_4O_6^{2-}$ species are seen to exhibit maxima in the range of 11 to 14% copper content (ligand ratio in the range of 3 to 4). The results thus suggest that the optimum activation of Cu(II) for the catalytic function probably occurs only when it is surrounded by a certain number of pyridine ligands.

Nishikawa and Tsuchida (*8*) studied the complexation of relatively low molecular weight PVP with Cu(II) in aqueous solution and from their potentiometric and spectroscopic results concluded that the four-coordinate Cu(II) complex is the main species formed, irrespective of the copper concentration in solution. In contrast to the monomeric pyridine–Cu(II) system, the stepwise formation constants, K_1 to K_4 in Eq. (1), increase with the number of coordinated ligands in the PVP system (*8*).

$$\begin{aligned} \mathrm{Cu} + \mathrm{L} &\overset{K_1}{\rightleftharpoons} \mathrm{CuL} \\ \mathrm{CuL} + \mathrm{L} &\overset{K_2}{\rightleftharpoons} \mathrm{CuL_2} \\ \mathrm{CuL_2} + \mathrm{L} &\overset{K_3}{\rightleftharpoons} \mathrm{CuL_3} \\ \mathrm{CuL_3} + \mathrm{L} &\overset{K_4}{\rightleftharpoons} \mathrm{CuL_4} \end{aligned} \qquad (1)$$

Thus the four stepwise formation constants, log K_i, are 1.1, 1.6, 2.7, and 4.7 for the Cu(II)-PVP (average MW 11,000) system as contrasted with 2.5, 1.9, 1.3, and 0.8 for the binding of pyridine by Cu(II). This has been explained by the high local concentration of ligands in the polymer domain with the result that once a copper ion is attached to one ligand of the PVP chain, the other ligands coordinate more readily. The above values of formation constants for the Cu(II) complexes with relatively low molecular weight PVP in aqueous solution may not be directly applicable to water-insoluble gels of high molecular weight PVP–Cu(II) complexes used as catalysts in the present work, since in gels the PVP chain is more densely contracted giving rise to greater steric hindrance. Furthermore, the crosslinks formed by the pyridine–Cu interaction would restrict the chain mobility and thus serve to isolate the units from each

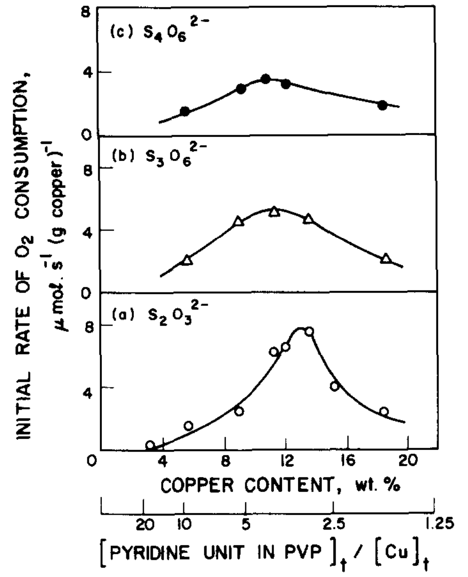

FIG. 2. Effect of copper content, or the ligand ratio of the complex, on the rate of oxidation, per unit weight of copper, of different polythionate species: (a) $S_2O_3^{2-}$; (b) $S_3O_6^{2-}$; and (c) $S_4O_6^{2-}$ at 30°C, 94.0 kPa O_2, and 50.0 mmol liter^{-1} polythionate concentration.

TABLE 1

Mole-Fraction Concentrations of Different Coordinate Species in PVP–Cu(II) Chelates Having Different Ligand Ratios

Ligand ratio[a]	[CuL]/[Cu]$_t$	[CuL$_2$]/[Cu]$_t$	[CuL$_3$]/[Cu]$_t$	[CuL$_4$]/[Cu]$_t$
1	0.0246	0.0026	0.0036	0.2398
2	0.0216	0.0031	0.0054	0.4887
3	0.0141	0.0026	0.0063	0.7396
4	0.0010	0.0002	0.0023	0.9954

[a] Ligand ratio = [pyridine units (L) in PVP]$_{total}$/[Cu]$_{total}$.

other in the gel matrix. However, the high local concentration of the pyridine units in the PVP gel matrix ought to offset any effect of restricted mobility. Therefore, the situation may be qualitatively viewed as similar both in a solution and in a gel. Thus, assuming that only up to four-coordinate species are formed, the concentrations of the various species in the PVP–Cu(II) water-swollen gels were calculated using the aforesaid formation constants for complexes in solution. The results are shown in Table 1 and plotted in Fig. 3.

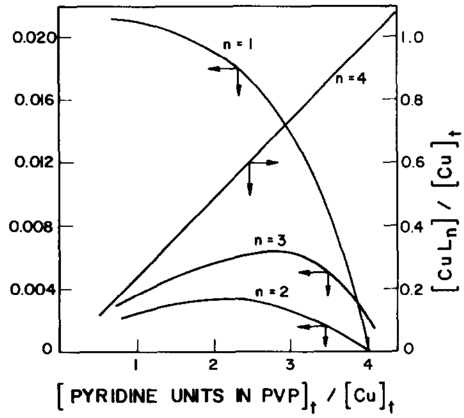

FIG. 3. Variation of the amounts of one-, two-, three-, and four-coordinate species with ligand ratio in PVP–Cu chelate (water-swollen gel), calculated from stepwise stability constants (*8*).

It is seen that the fraction of the four-coordinate Cu complex increases and that of the one-coordinate complex decreases monotonically with the increase in the ligand ratio, while both the two-coordinate and the three-coordinate complexes pass through a maximum as the ligand ratio is increased. The results presented in Fig. 2 can thus be explained by assuming that only the two- and three-coordinated PVP–Cu(II) complexes are catalytically active for the oxidation of thiosalts by molecular oxygen, while both the one- and four-coordinated complexes, though coordinatively unsaturated, are catalytically inactive. The activation of the complexed Cu(II) ion thus seems to depend on the number of ligand neighbors around the ion.

To test the above hypothesis, we prepared a 1 : 1 complex of Cu(II) with 2,2′-bipyridine (*9*). The degree of metal–ligand interaction in this complex, as represented by the wavenumber shift (20 cm^{-1}) in the absorption due to $\nu_{C=C,C=N}$ of a pyridine ring, is similar to that in the PVP–Cu(II) complex ($\Delta\nu_{C=C,C=N}$ = 17 cm^{-1}). This bidentate Cu(II) complex was, as expected, found to be highly active for the oxidation of $S_2O_3^{2-}$ to SO_4^{2-} by molecular oxygen, the initial rate at 30°C being about 10 times faster as compared to the PVP–Cu(II) complex. Unlike the latter, however, it did not catalyze the oxidation of $S_3O_6^{2-}$ and $S_4O_6^{2-}$ ions. This seems to suggest that a three-coordinate Cu(II) complex with pyridine ligand which has an appropriate degree of metal–ligand interaction would be active for the oxidation of $S_3O_6^{2-}$ and $S_4O_6^{2-}$ ions. The tridentate complex of Cu(II) with 2,2′,2″-terpyridine was, however, found to be catalytically inactive with regard to the oxidation of all the aforesaid polythionate species by molecular oxygen. This can be attributed to a high degree of metal–ligand interaction in this complex, as evidenced by a large shift (~55 cm^{-1}) in the absorption due to $\nu_{C=C,C=N}$. The striking contrast between the Cu(II) complexes with 2,2′-bipyridine and 2,2′,2″-terpyridine is also highlighted by their oxidation–reduction potential values (*10*) of +120 and −80 mV, respectively, indicating that the terpyridine stabilizes the cupric relative to the cuprous state more effectively than does bipyridine. From the above discussion we conclude that besides coordinative unsaturation, proper ligand environment (type and number of ligands around metal ion) and a proper degree of ligand–metal interaction are necessary in order to achieve the desired catalytic function.

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