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Studies on the Reaction of CN^- with (Tetradentate α-amine oxime)copper(II) Complexes

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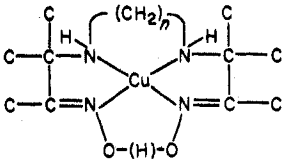
The association of CN^- with $Cu(PnAO\text{-}H)^+$ and $Cu(EnAO\text{-}2H)^0$ to form the monocomplex in alkaline media is reversible over a short period of time and gives values of $-\Delta G° = 4.2 \pm 0.1$ and 6.3 ± 0.3 kcal/mol, $-\Delta H° = 10.6 \pm 0.4$ and 17.0 ± 0.2 kcal/mol, and $-\Delta S° = 22 \pm 1$ and 43 ± 4 eu, respectively, at 25 °C and $I = 0.1$. Some evidence was found spectrally for the weak association of a second CN^- to the EnAO complex. Association of CN^- with the PnAO complex shifts the absorption maximum from 504 to 590 nm while with the EnAO complex the shift is from 609 to 575 nm. This difference is related to the complex charge and the lack of the intramolecular H bond in the latter system. With an excess of CN^- an irreversible reaction takes place over a longer period of time, in which the mixed complex decomposes to $Cu(CN)_3^{2-}$, OCN^-, CH_3CN, either EnAO or PnAO, and other degradation products of the ligand. No cyanogen is observed. Surprisingly, CH_3CN is formed from the tetradentate ligand and not from the cyanide ion as shown by isotopic measurements. A quantitative study of the amount of CH_3CN and PnAO (or EnAO) produced was made. The kinetics of the irreversible reactions of the mixed complexes with excess CN^- was studied and tentative mechanisms suggested.

Introduction

Over the years there has been a steadily increasing interest in the coordination chemistry of copper ion,[3] due in part to its catalytic properties in biological systems.[4] Multidentate ligand–copper(II) complexes are especially interesting model systems. Their study is expected to aid in understanding the more complex natural systems. Much of the catalytic activity appears to be related to the cyclic interconvertibility of copper(I) and copper(II).[5] However, the redox cycle and the usual high lability of both copper species has made progress on determining the mechanisms of these reactions very slow.

The complexes selected for this mechanistic study are two (tetradentate α-amine oxime)copper(II) ions of high thermodynamic stability whose crystal structure has either been done or can be inferred from similar structures.[6,7] They have the arrangement[8]



(where $n = 2$ for EnAO and $n = 3$ for PnAO). The stability of the hydrogen bond is closely related to the value of n. In the alkaline region used in this study, the PnAO complex is almost entirely in the hydrogen-bonded form and has a charge of +1 while the EnAO complex has a charge of zero and no internal hydrogen bond. Reaction of these complexes with CN^- was chosen for study because CN^- is one of the few ligands bound strongly enough to replace the tetradentate ligand at mild stoichiometric excesses and oxidation of CN^- was anticipated which would give Cu(I) as $Cu(CN)_3^{2-}$, preventing the backward reaction and also preventing the disproportionation of Cu(I). Little kinetic information is available on the CN^- reaction with copper(II) complexes. Duke and Courtney[9] studied the kinetics of the $Cu(NH_3)_4^{2+}$–CN^- reaction in concentrated NH_3 solution and Tanaka et al.[10] used $CuEDTA^{2-}$ with CN^-. Several attempts have been made with the rapid $Cu(OH_2)_4^{2-}$–CN^- reaction.[11] These did not provide a rational, unified mechanism for the basic reaction and, in fact, did not agree on the type of species involved in the rate-determining step leading to the products. The relative slowness of the CN^- reaction with the PnAO and EnAO complexes allows precise studies on some of the intermediates, the products, and the reaction rates under a variety of solution conditions and provides considerable information about the mechanism of reaction.

In this paper we report equilibrium studies on the association of CN^- with two copper(II) complexes in the first stage of reaction and stoichiometric studies, mechanistic information derived from isotopic transfer experiments, and kinetic studies on the second, irreversible reaction with CN^-. The two complexes are markedly different in their behavior, the stoichiometry far from what was anticipated, and the kinetic rate expressions of enough detail to allow considerable insight into the mechanism of reaction.

Experimental Section

The ligands PnAO and EnAO were prepared as previously described[12] and recrystallized as the free amine. Their IR spectra in the 4000–700-cm^{-1} region agree with previously analyzed samples. Copper complexes were prepared using the usual methods with the precaution that the pH during formation and recrystallization was held at 2.3 for $Cu(EnAO)^{2+}$ and 8.0 for $Cu(EnAO\text{-}H)^+$. Normally the anion was ClO_4^-, but when others were required, they were prepared by anion exchange with an excess of Dowex 50W-X resin in the appropriate state. Analysis for CHN and halogen was commercial, copper and molecular weight by standard methods, and H_2O by Karl Fisher titration (Brinkmann—Automat E547).

Anal. Calcd for $[Cu(PnAO\text{-}H)]ClO_4 \cdot H_2O$: $C_{13}H_{29}O_7N_4CuCl$, fw 452.4: C, 34.52; H, 6.46; N, 12.38, H_2O, 4.0. Found: C, 34.05; H, 6.67; N, 12.30; H_2O, 4.1. Calcd for $[Cu(PnAO\text{-}H)CN] \cdot H_2O$: $C_{14}H_{27}O_2N_5Cu$, fw 379.0: C, 44.37; H, 7.71; N, 18.48; H_2O, 4.8. Found: C, 43.99; H, 7.64; N, 18.31; H_2O, 4.8. Calcd for $[Cu(EnAO\text{-}H)]ClO_4$: $C_{12}H_{25}O_6N_4CuCl$; fw 420.4: C, 34.29; H, 6.00; N, 13.33; Cl, 8.43; H_2O, 0.0. Found: C, 35.75; H, 6.30; N, 12.80; Cl, 8.35; H_2O, 0.02. Calcd for $[Cu(EnAO)](ClO_4)_2$: $C_{12}H_{26}O_{10}N_4CuCl_2$, fw 520.8: Cu, 12.20. Found: Cu, 12.22.

The charge on a complex ion was determined by its absorption characteristics on a Dowex 50W-X4 or 1-X8 resin in the appropriate ionic form. With the CN^- complexes, excess CN^- was present to prevent dissociation. Using this method, one could determine the sign of the charge (+, –, or 0) but not its magnitude. Nonlabile complexes of Ni(II) of known charge were used as standards and in the cases reported, the sign of the charge was unambiguous.

Visible and UV spectra were obtained with Cary 14 or 15 spectrophotometers at a constant temperature ±0.05 °C. Solvent water was deionized and doubly distilled. All solutions used for spectral or K_f measurements were protected from the atmosphere to prevent CO_2 absorption. Recrystallized NaCl and $NaNO_3$ were often used for ionic strength control since the solubilities of the complex perchlorates were often too low to be useful. Standard NaOH solutions were freed of CO_3^{2-} by filtering concentrated solutions and diluting with CO_2-free water. Solutions of recrystallized NaCN were analyzed argentometrically and were protected from atmospheric CO_2.

All studies, unless otherwise noted, were carried out in the basic region pH 9–12, to lessen the corrections for CN^- hydrolysis. In this range, essentially no free Cu^{2+} or tetradentate ligand exists in equilibrium with the complex ion. In basic solution, pH ~10, the complexes are in the forms $Cu(PnAO\text{-}H)^+$ and $Cu(EnAO\text{-}2H)^0$ [13] and combine with CN^- to form only $Cu(PnAO\text{-}H)CN^0$ and $Cu(EnAO\text{-}2H)CN^-$ as shown by Job's method and by the agreement with the theoretical potentiometric formation of curves.

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The molar absorbances for the complexes in each of their acid–base forms were determined by conventional pH–spectral measurements at constant temperature. However, the molar absorbances of the CN^- adducts obtained in this way could not be relied upon since irreversible decomposition took place rapidly with large excesses of CN^-. The special methods used in these cases are explained in the Results.

The formation constants for the mixed complexes, i.e., $Cu(PnAO\text{-}H)CN^0$ and $Cu(EnAO\text{-}2H)CN^-$, were determined by measuring the $[CN^-]$, pH, and spectra of solutions of known initial composition. The $[CN^-]$ was determined with a Chemtrix S/N-258 specific ion electrode and an Orion 601 amplifer meter standardized before and after each run. Suitable conditions were found where less than 1% replacement of coordinated PnAO or EnAO occurred during equilibration. The equilibration of CN^- with both complexes to form the mixed species was shown to have a $t_{1/2}$ of less than 5 ms at 25 °C by stopped-flow spectral measurements using a conventional Durrum apparatus. Correction for the HCN present due to hydrolysis at various temperatures was made using thermodynamic data.[14]

The standard enthalpies of formation of the cyano adducts, i.e., $Cu(PnAO\text{-}H)^+ + CN^- \rightarrow Cu(PnAO\text{-}H)CN^0$, were determined calorimetrically in a simple insulated apparatus. Typically, a ΔT of 2 °C was observed for the concentrations used with an uncertainty of ±0.002 °C. The calorimeter was standardized with the HCl–KOH reaction (0.1 M), and corrections were made for heats of dilution, excess reagents, and incomplete complex formation where necessary. $\Delta H_f°$ was also obtained from the temperature dependence of K_f. However, as has been noted often in similar circumstances, these values are considerably less accurate and precise than those directly determined.

Products of Reaction. Analysis of the gaseous products for $(CN)_2$ was carried out by mass spectral analysis and by gas-phase chromatography. Standard $(CN)_2$ was prepared by the reaction of $HgCl_2$ and $Hg(CN)_2$ at 400 °C. The mass to charge values of 52, 26, 12, 38, 24, 14, 64, and 66 (in decreasing order of abundance) gave a clear quantitative and qualitative analysis. In the basic media employed, $(CN)_2$ was never seen as the product of the reaction of the complexes with excess CN^- by either mass spectrometry or gas-phase chromatography using N_2 flow or vacuum techniques. Reaction of CN^- with $Cu(aq)^{2+}$ without added base or buffer gave copious amounts of $(CN)_2$.

Reaction of either complex with excess CN^- did give a substance which was partially volatile under vacuum conditions. Its main mass spectral peak was at m/e 41 and from its fragmentation pattern, it was CH_3CN [m/e (intensity) 41 (100), 40 (52), 39 (19), 38 (12), 14 (11), 12 (5)]. $Cu(aq)^{2+}$–CN^- did not produce this substance nor did the free ligand in the presence or absence of strong base. Quantitative analysis for the ratio (CH_3CN produced:complex decomposed) was determined by isotope dilution using $CH_3{}^{14}CN$. The source of CN in the CH_3CN produced was determined by ^{14}C tracer studies utilizing both $^{14}CN^-$ and $CH_3{}^{14}CN$. These substances were present during separate reactions of CN^- with the copper complexes. After reaction, CH_3CN was extracted with ether, washed with acid and base solutions, dried, reduced with $LiAlH_4$, distilled quantitatively into aqueous HCl, brought to dryness, and the thiourea derivative made and recrystallized. Radioactivity was measured by liquid scintillation counting with a Nuclear Chicago 720 system. The counting efficiency was nearly 50% and the samples were normally in the 10 000–20 000-cpm range.

Analysis of reaction mixtures for OCN^- was made by the method described by Snell and Snell.[15] It consisted of acidifying the solution for exactly 10 min at pH 1 giving NH_4^+ and HCOOH (a blank correction has to be made for the CN^- present) and quenching the mixture by converting to pH 7.2. The NH_4^+ was isolated on a cation-exchange column at 15 °C and eluted with dilute base, and the NH_3 was quantitatively determined spectrally using Nessler's reagent. Standards reproduced to ±3% and the complexes of $Cu(aq)^{2+}$ and ligand did not interfere.

Analysis for unreacted tetradentate ligand after the CN^- reaction with complex was carried out by volatizing CN^- as HCN and oxidizing Cu(I) by *alternatively* bubbling CO_2 and air through the solutions for 3 days. After the solution was filtered, the pH was altered to 10.5 for PnAO and 7.2 for EnAO where $Cu(PnAO\text{-}H)^+$ and a mixture of $Cu(EnAO)^{2+}$ and $Cu(EnAO\text{-}H)^+$ exist. Using the molar absorbancies of the PnAO complex at 504 nm and an isosbestic of the two EnAO complexes at 600 nm, the concentration for a known volume of solution was determined. Under the conditions involved, the complexes are fully formed (±0.5%). No evidence was seen for complex formation of Cu(II) with the residues from decomposed PnAO or EnAO at these pH's.

The CN^- stoichiometry could not be determined by measuring the residual CN^- with a CN^--specific electrode because of its lack of sensitivity at the high excesses needed for complete reaction. Therefore, a structurally similar complex $Cu(BnAO\text{-}H)^+$ ($n = 4$) of less stability (both thermodynamically and kinetically) was used to determine the reacting ratios. When a known amount of CN^- was added to a solution containing a known amount of $Cu(BnAO\text{-}H)^+$ the monocyano complex forms but is highly unstable and quickly disappears. After a few moments, the excess CN^- was determined by the CN^- electrode and the absorbance was read at several wavelengths. Over a range of 10–95% complex decomposition, with an excess of complex, 3.5 CN^- were used per copper complex. This corresponds to the expression

$$H_2O + 2Cu(BnAO\text{-}H)^+ + 7CN^- \rightarrow OCN^- + 2Cu(CN)_3{}^{2-} + 2BnAO$$

and strongly suggests $Cu(CN)_3{}^{2-}$ as one of the major products, in agreement with the literature.[16] Hydrolysis of BnAO to give CH_3CN, acetone, and other products would not change this result. It is suggested and seems likely that BnAO, PnAO, and EnAO complexes will show the same overall CN^- stoichiometry.

Kinetics of Reaction. The reaction of these complexes with CN^- takes place in two steps. The first is extremely rapid and results in the addition of one CN^- to the complex without rupture of the tetradentate ligand–copper bonds (vide infra X-ray structure). This reaction is too rapid to be followed by stopped-flow methods.

$$Cu(AO) + CN^- \rightleftarrows Cu(AO)(CN)^{17}$$

The second step is much slower and shows the stoichiometry

$$\text{PnAO:}\quad 2CuAO(CN)^0 + 5CN^- + H_2O \rightarrow 2Cu(CN)_3{}^{2-} + OCN^- + 1.4PnAO + 1.2CH_3CN$$

$$\text{EnAO:}\quad 2CuAO(CN)^- + 5CN^- + H_2O \rightarrow 2Cu(CN)_3{}^{2-} + OCN^- + 1.2EnAO + 0.8CH_3CN$$

In the kinetic studies of these reactions it was possible to use conventional techniques for the slower reacting PnAO system, but the stopped-flow technique was needed for the EnAO system. Trials for the PnAO system consisted of adding microliter amounts of a CN^- stock solution to the complex solution. The light absorption of the solutions of the monocyano complex was followed as a function of time with the first reading being approximately 15 s after mixing. Reactants for the EnAO system were of equal volume, and mixing times were essentially zero (~4 ms) relative to the reaction time. Ionic strengths were maintained constant with purified $NaNO_3$, NaCl, or $NaClO_4$. The pH (phosphate ion buffer) and temperature were maintained constant.

Kinetic data were collected by observing the disappearance of the mixed complexes at 590 nm (ϵ 425 cm^{-1} M^{-1}) for the PnAO system and at 575 nm (ϵ 389 M^{-1} cm^{-1}) for the EnAO complex. Only in the samples with the very lowest total $[CN^-]$ was the Cu(PnAO-H)CN mixed complex not completely formed at the time of mixing, and so an appropriate correction had to be made.

Rates were measured either by a (a) direct measurement from the recorder tracings using a derivimeter, (b) calculation assuming linearity over a small region (if applicable), or (c) by computer techniques. All three methods correlated excellently with each other. The kinetic data are reported such that the ± values represent one standard deviation.

Results

The (α-amine oxime)copper(II) complexes can exist in three acid–base forms by the successive ionization of oxime hydrogens: $Cu(AO)^{2+}$, $Cu(AO\text{-}H)^+$, or $Cu(AO\text{-}2H)^0$. A large pH range of stability for the +1 charged species is usually found since it has an intramolecular bond. However, steric strain in the EnAO system caused by the ethylene bridge prevents close approach of the oxime oxygens and, therefore, a weak hydrogen bond. Thus, the major species at pH 9–12 in the EnAO system is $Cu(AO\text{-}2H)^0$ and not $Cu(AO\text{-}H)^+$ as found in the PnAO system. Large spectral changes accompany these ionizations as is shown in Table I.

Cyanide ion also causes significant spectral changes which are shown in Figure 1, and it was demonstrated conclusively

Table I. Spectral Data for Complexes[a]

compound	$\lambda_{\max}$, nm	ϵ, cm^{-1} M^{-1}
$Cu(EnAO)^{2+}$	520	288
$Cu(EnAO-H)^+$	420	222
$Cu(EnAO-2H)^0$	629	338
$Cu(EnAO-2H)CN^-$	575	431
$Cu(PnAO-H)^+$	504	213
$Cu(PnAO-H)CN^0$	580	426

[a] In water at 25 °C. Isosbestics (λ, ε): Cu(EnAO-2H)-$Cu(EnAO-2H)(CN)^-$: 694, 171; 609, 328. $Cu(PnAO-H)^+$-$Cu(PnAO-H)(CN)^0$: 525, 200; 420, 35.

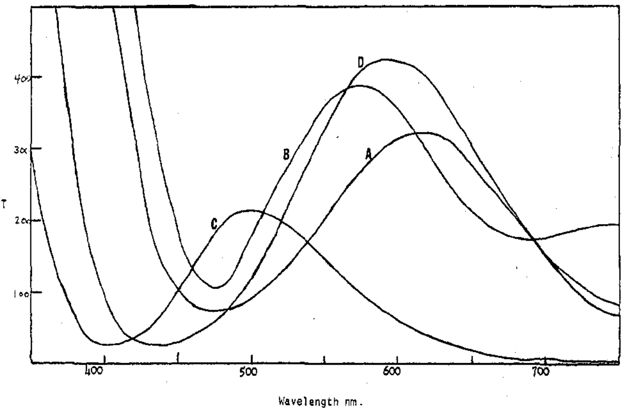


Figure 1. Absorption spectra of complexes: A, $Cu(EnAO-2H)^0$; B, $Cu(EnAO-2H)CN^-$; C, $Cu(PnAO-H^+$; D, Cu(PnAO-H)CN.

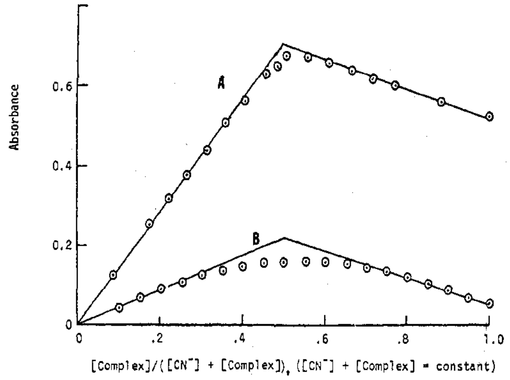


Figure 2. Job graphs for the formation of (A) $Cu(EnAO-2H)CN^-$ (pH 12, $I = 0.1$, 760 nm) and (B) $Cu(PnAO-H)CN^0$ (pH 12, $I = 0.1$, 625 nm).

that only one species formed with each complex by the invariance of the isosbestics, by Job's method, Figure 2, and by potentiometric formation curves. The mixed complex formation reactions are rapid with $t_{1/2} < 5$ ms. The sharpness at the equivalence point of the Job's plots for the EnAO system points out the greater thermodynamic stability of this cyano complex over that of PnAO. In agreement with the 1:1 stoichiometry was the isolation of $[Cu(PnAO-H)(CN)]\cdot H_2O$ and the subsequent single-crystal X-ray structure showing the copper ion to be in a tetragonal-pyramidal geometry with the H_2O uncoordinated. This structure did not properly converge to a low R value due to partial twinning in all of the crystals found. However, the basic structure emerged easily from the Fourier diagrams.

Figure 3 gives a graph of the $[CN^-]_{free}$ compared to that added for both complexes confirming the higher stability of $Cu(EnAO-2H)CN^-$. In obtaining the data for Figures 1–3, care was taken to measure the spectra and record the $[CN^-]$ before any appreciable amount of the secondary reaction could take place by the use of rapid mixing, short periods of contact, and low temperatures.

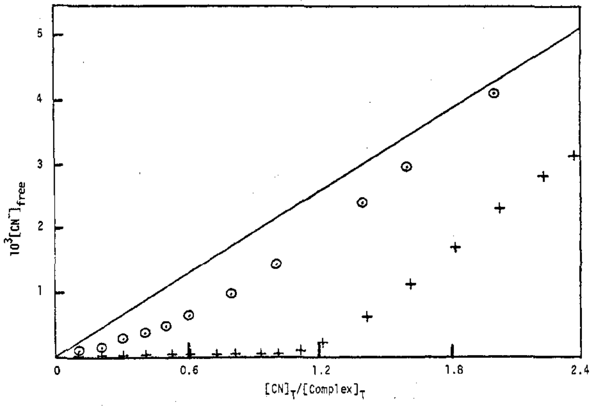


Figure 3. Titration of a 2.02×10^{-3} M solution of $Cu(PnAO-H)^+$ (○) and of a 2.47×10^{-3} M solution of $Cu(EnAO-2H)^0$ (+) with 0.1006 M NaCN. Line respresents $[CN^-]_{free}$ expected in absence of complex (pH 11.5 $T = 19.5$ °C, $I = 0.10$).

The molar absorbancies of the complexes at selected wavelengths obtained by spectral measurements of solutions containing a large excess of CN^- could not be trusted due to the possibility of AO replacement by NC^- (decomposition) during mixing or during the time used for measurement. Decomposition is appreciable for the EnAO system even at mild excesses of CN^-. To avoid this, the molar absorbancies and formation constants were obtained at low $[CN^-]$ by graphical means. Three techniques were used: Baker et al.[18] and Rose and Drago[19] for only spectral data and by an expression derived for use with a combination of spectral and $[CN^-]$ data. While all methods converged on the same approximate solutions, the Rose and Drago method gave the best fit to the data in the PnAO system. Utilizing the expression

$$1/K_f = \frac{A - A_0}{\epsilon_{\text{mixed}} - \epsilon_{\text{free}}} - [C]_T - [CN]_T + \frac{[CN^-]_T[C]_T(\epsilon_{\text{mixed}} - \epsilon_{\text{free}})}{A - A_0} \qquad (1)$$

where A is the absorbance of a solution, $[C]_T$ is the total concentration of the complex, and ϵ is the molar absorbancy of either the mixed or free complex. Data sets of A, $[C]_T$, A_0, and $[CN^-]_T$ converged sharply giving values of $K_f \approx 1300$ and $\epsilon_{\text{mixed}} \approx 450$. The ϵ_{free} of the beginning complex was determined directly. Application of this technique to the EnAO system, while satisfactorily producing a value for ϵ_{mixed}, did not define K_f as precisely due to its large value. To confirm the PnAO values by an independent method the apparent molar absorbancies ϵ_T and $[CN^-]_{free}$ were measured on a series of solutions containing complex and CN^-. The latter measurement was made with a cyanide electrode. It can be shown that

$$\epsilon_T = \frac{\epsilon_0 + \epsilon_1 K_f[CN^-]}{1 + K_f[CN^-]} \qquad (2)$$

or, at low $K_f[CN^-]$ (PnAO system only)

$$\epsilon_T = \epsilon_0 + \epsilon_1 K_f[CN^-] \qquad (3)$$

Graphs of ϵ_T vs. $[CN^-]_{free}$ were linear and gave excellent agreement with the previously obtained values of ϵ_0 and $\epsilon_1 K_f$.

On the question of how many CN^-'s are added to the complex, a plot of log $(\epsilon_T - \epsilon_0)$ vs. log [CN] was highly linear in the PnAO system (Figure 4) with a slope of 1.00 ± 0.05. Thus, eq 3 is followed and only one CN^- is added to the complex in this range of $[CN^-]$. An additional illustration of this is given in Figure 5 where $\bar{n}$ (from spectral data) is compared with the ratio of CN^- added to complex (CN^--

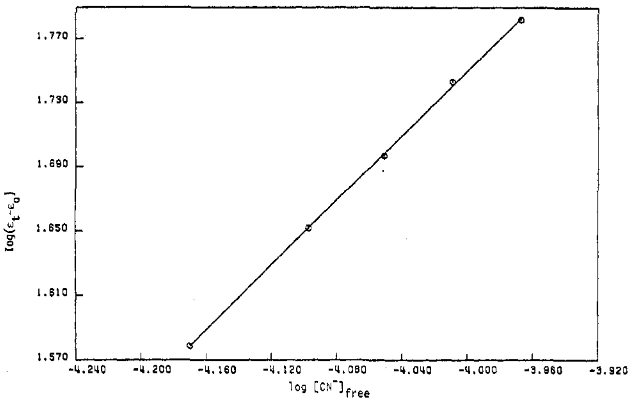


Figure 4. Formation of Cu(PnAO-H)(CN)^0; graph of eq 3 ([complex]$_t$ = 2.02 × 10^{-3}, T = 19.0 °C, I = 0.10, pH 11.5).

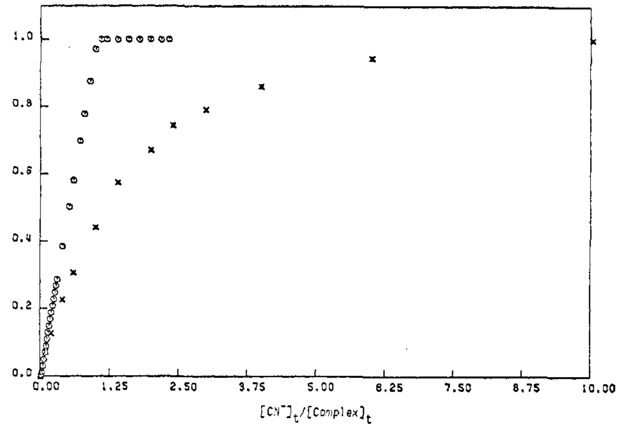


Figure 5. Average number of CN$^-$ bound per complex, $\bar{n}$, vs. [CN$^-$]$_t$/[complex]$_t$ ratio: top curve, Cu(EnAO-2H)^0; bottom curve, Cu(PnAO)-H$^+$. [complex] ≈ 1 × 10^{-3} M, pH 11.5, I = 0.10, T = 20 °C.

electrode data) which produced an analogous plot. At a 1:1 ratio the EnAO complex is nearly completely formed and no further spectral change takes place while the PnAO complex is less stable and approaches a 1:1 ratio only at high CN$^-$ concentrations. A summary of the derived molar absorbancies and isosbestic points in these two systems is given in Table I.

Formation Constants. For both systems, three methods were tried: (a) spectrophotometric evaluation, (b) spectra and CN$^-$ concentration determination, and (c) CN$^-$ determination only. In each case, values were obtained which were consistent with the other methods. For the PnAO system, the most precise method involved using spectral data alone to evaluate the values of R and [CN$^-$]$_{\text{free}}$. If R = [Cu(PnAO-H)CN^0]/[Cu(PnAO-H)$^+$], then $R = K_f$[CN$^-$]. Values of R were obtained at several wavelengths from the known molar absorbancies and the initial formal concentrations, and [CN$^-$] was the difference between that used and that put in or measured directly. A correction for the hydrolysis of CN$^-$ was made. Figure 6 shows the results of two titrations, and K_f was obtained from this slope. For comparison, the expression

$$\epsilon_T = \frac{\epsilon_0 + \epsilon_1 K_f[\text{CN}^-]_{\text{free}}}{1 + K_f[\text{CN}^-]_{\text{free}}} \qquad (4)$$

can be derived, where ϵ_T, ϵ_0, and ϵ_1 are the solution, complex, and cyano complex molar absorbancies. Thus, the apparent solution molar absorbancies change with [CN$^-$]$_{\text{free}}$ (from CN$^-$-electrode data), in a fashion shown in Figure 7. From nonlinear least-squares evaluations of sets of data to eq 4, the fit shown in Figure 7 (Cal-Comp line) gave values of ϵ_0 = 67.2 ± 0.7 M^{-1} cm^{-1}, K_f = 1851 ± 16 M^{-1}, and ϵ_1 = 425 ± 5 M^{-1} cm^{-1} in excellent agreement with results obtained independently.

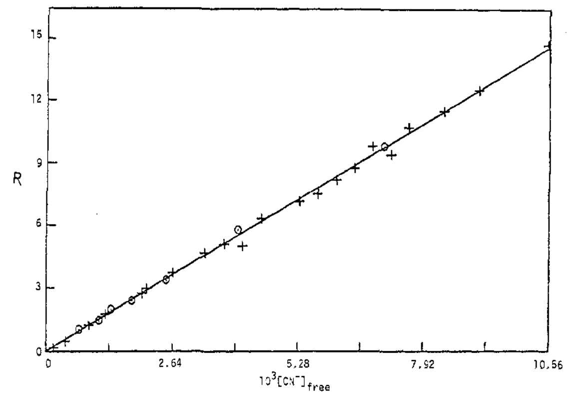


Figure 6. Formation of Cu(PnAO-H)CN^0. Spectral data only, R = [Cu(PnAO-H)CN^0]/[Cu(PnAO-H)$^+$]. [complex] = 1.02 × 10^{-3} M, T = 20 °C, I = 0.10. X and O are independent determinations.

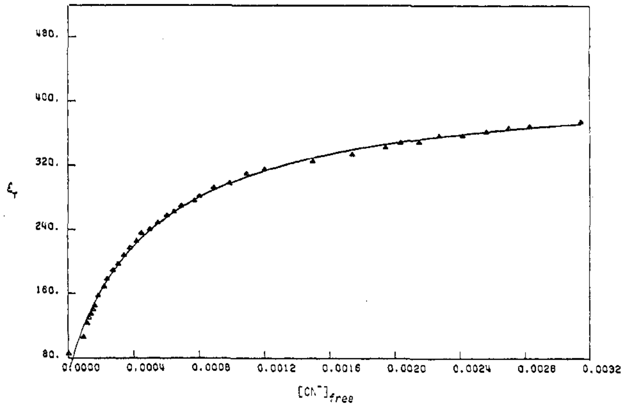


Figure 7. Fit of eq 4 to a combination of spectrophotometric and potentiometric data for the Cu(PnAO-H)(CN)^0 system. pH 11.5, T = 20 °C, I = 0.10.

It was found that the CN$^-$-electrode data gave best precision for the EnAO system because the spectral changes were small and the formation constant was large. For solutions of CN$^-$ at the proper pH and ionic strength, the [CN$^-$] in the presence and absence of Cu(EnAO-2H)^0 was determined. From this, all of the terms in K_f could be calculated. Over a range of 5–90% complexation, K_f was constant. It was also independent of pH in the region 11.0–11.7. Table II lists the final values of K_f for both systems.

The enthalpy change in the formation of the cyano complexes measured calorimetrically at 25 °C, pH 11.5, and I = 0.1 was −10.6 ± 0.2 kcal/mol for Cu(PnAO-H)CN^0 and −17.0 ± 0.2 kcal/mol for Cu(EnAO-2H)CN$^-$. These are to be compared with the values −8.6 ± 0.4 and −19.0 ± 0.2, kcal/mol respectively, which were obtained from the less precise K_f variation with temperature. Using the calorimetric enthalpy change gives the thermodynamic values for cyano complex formation for PnAO and EnAO at 25 °C respectively as follows: $\Delta G°$ = −4.2 ± 0.1, −6.3 ± 0.3 kcal/mol; $\Delta H°$ = −10.6 ± 0.4, −17.0 ± 0.2 kcal/mol; $\Delta S°$ = −22 ± 1, −43 ± 4 eu.

Stoichiometry. In the presence of excess CN$^-$ the second, slower reaction takes place which results in the generation of colorless copper(I) cyano complexes by displacement of the amine oxime ligand. The kinetics of these reactions can conveniently be studied by following the spectral changes which occur, and these will be described after the stoichiometric studies.

Initially, we considered this reaction to be a displacement of AO by CN$^-$ followed by the reaction of CN$^-$ with Cu(II).

Table II. Formation Constants for Cu(AO)CN-Type Complexes

T, °C	pH	I	K_f, M^{-1}
A. $Cu(PnAO\text{-}H)^+ + CN^- \overset{K_f}{\rightleftharpoons} Cu(PnAO\text{-}H)CN^0$			
25.0	9.95	0.10	1340 ± 54
25.0	10.55	0.10	1212 ± 57
25.0	10.98	0.10	1240 ± 24
25.0	11.51	0.10	1207 ± 43
25.0	12.02	0.10	989 ± 35
10.00	10.98	0.10	2768 ± 6
15.1	10.98	0.10	2084 ± 46
20.1	10.98	0.10	1396 ± 17
25.1	10.98	0.10	1240 ± 24
30.1	10.98	0.10	945 ± 3
35.0	10.98	0.10	809 ± 2
25.0	11.5	0.50	736 ± 9
25.0	11.5	0.16	1024 ± 29
25.0	11.5	0.10	1151 ± 25
25.0	11.5	0.05	1228 ± 29
25.0	11.5	0 (calcd)	1460
B. $Cu(EnAO\text{-}2H)^0 + CN^- \overset{K_f}{\rightleftharpoons} Cu(EnAO\text{-}2H)CN^-$			
20.0	11.5	0.10	$(3.9 \pm 1.2) \times 10^4$
0.8	11.0	0.10	$(4.4 \pm 0.7) \times 10^5$
0.8	11.3	0.10	$(4.3 \pm 2.3) \times 10^5$
0.8	11.7	0.10	$(3.7 \pm 0.5) \times 10^5$

Cyanogen is one of the main products of the reaction of $Cu(aq)^{2+}$ with CN^-, and it is often stated that it is generated even in basic media. However, $(CN)_2$ reacts with aqueous base to produce a highly colored (yellow) azulmic acid of unknown structure. Reaction of either of the Cu(AO)CN complexes with CN^-, concentrated or dilute, did not produce any $(CN)_2$ in the pH range 8–12, only OCN^-. The detection limit of 0.01% of theoretical is estimated. Two possibilities arise: (a) $(CN)_2$ is formed and reacts to give OCN^- and CN^- and/or azulmic acid or (b) OCN^- is formed directly. The reaction of $(CN)_2$ with basic solution in the presence or absence of complex gave the spectrum of azulmic acid (peak at 405 nm) while reaction of CN^- with the complexes did not produce this characteristic spectrum and, in fact, the product solutions were colorless. Thus, OCN^- is directly formed in the main reaction and does not go through $(CN)_2$.

While $(CN)_2$ was not produced in the reaction, a volatile substance (at −78 °C (10^{-3} mm)) was formed which had a formula weight of 41 and proved to be CH_3CN. Identity was established by mass spectral comparison with a known sample, ^{14}C isotope dilution experiments, and vapor pressure chromatography retention time studies. A quantitative determination of the CH_3CN yield utilized $CH_3{}^{14}CN$ prepared from $K^{14}CN$. The specific activity of the KCN solutions was determined by AgCN precipitation, and the exchange rate between CH_3CN and $^{14}CN^-$ was found to be less than 0.3% in 20 h at 25 °C. The specific activity of the $CH_3{}^{14}CN$ was determined using the purified phenylthiourea derivative produced as given below. The question of whether the CN group in CH_3CN comes from CN^- was unambiguously settled by conducting the reaction of the complexes with $^{14}CN^-$, isolating the CH_3CN formed after adding carrier, and measuring the specific activity of the purified CH_3CN. On the basis of one CH_3CN per complex decomposed, less than 1.0 ± 0.5% of the CH_3CN was formed using CN^-. Thus, the carbons in CH_3CN must both come from the PnAO or EnAO ligands. The determination of the yield of CH_3CN per mole of complex reacted utilized $CH_3{}^{14}CN$. After reaction with CN^-, $CH_3{}^{14}CN$ of known amount and activity was added, and the CH_3CN was isolated and purified. It was reduced to ethylamine, converted to the phenylthiourea derivative, and recrystallized, and its specific activity was determined by liquid scintillation counting. In three runs using the PnAO system, covering a reaction time of 0.13–9.3 h, 0.60 ± 0.05 mol of CH_3CN was produced per mole of complex reacted while 0.30 ± 0.03 was the ratio in the EnAO system. In blank experiments it was established that less than 1% CH_3CN was generated by contact of NaCN with PnAO or EnAO under the same conditions. Also, no CH_3CN is formed by contact of base with the complex in the absence of CN^-.

Table III. Reaction of Complexes with CN^-: OCN^- Yield[a]

	no. of detns	$10^4[OCN^-]$-found	complex used: OCN^- found
$Cu(PnAO\text{-}H)^+$	6	0.86 ± 0.04	1.98 ± 0.06
$Cu(EnAO\text{-}2H)^0$	6	0.89 ± 0.05	2.02 ± 0.12

[a] Conditions: pH 12, T = 25 °C, [complex] = 1.74×10^{-4} M, [NaCN] = 0.435 M.

Table IV. Recovery of Tetradentate Ligand

10^4[ligand], M	10^3[complex], M	$[CN^-]$, M	no. of runs	% recovered
1.515 (PnAO)	0	0.487	5	101.6 ± 3.6 (blank)
3.967 (EnAO)	0	0.487	4	94.5 ± 2.4 (blank)
0	5.2–0.87 (PnAO)	0.389	6	73 ± 10
0	2.96–1.97 (EnAO)	0.339	6	61 ± 3

Analysis of the (OCN^- formed:complex consumed) ratio was conducted with calibrations being made for the efficiency of NH_3 recovery (~94%) and the degree of CN^- hydrolysis (~1/2%). Table III summarizes the results. These clearly show that in both systems the molar ratio [complex]/$[OCN^-]$ equals 2.0 and thus, the overall oxidation–reduction process is $2Cu^{II} + CN^- + 2(OH^-) \rightarrow 2Cu^I + H_2O + OCN^-$.

After the complexes react with CN^- and become colorless, they can be partially regenerated by removal of CN^- as HCN and metal ion oxidation with air. Studies proved that all HCN could be removed and all the copper ion oxidized by alternate CO_2–air treatment for 3 days. Other ligands, resulting from partial decomposition of the parent ligands, were shown not to produce colored compounds with Cu(II) at the stated pH's. Thus, the regenerated Cu(II) complex could be used as a measure of the undecomposed ligand. In separate tests it was shown that the ligands are stable under these conditions. The results of these studies are shown in Table IV. Decomposition of the complex by OH^- alone was shown to displace the ligand but it is entirely recoverable, ±2%.

Cyanide Ion Stoichiometry. Both the EnAO and PnAO complexes required excesses of CN^- to go to completion and, thus, only a small change in $[CN^-]$ occurred due to reaction. Since the Cu(I)–CN^- complexes are labile, the excess CN^- had to be determined without separation. An analogous complex, which is less stable, is $Cu(1,4\text{-}BnAO\text{-}H)^+$. Addition of CN^- to this complex gave the initial blue color of the monocyano complex which was rapidly lost. Analysis of the complex spectra, ϵ 180 M^{-1} cm^{-1} at 540 nm, showed no change in the peak position or the shape of the spectrum after equilibration with small amounts of CN^- but did show a diminished intensity. This suggests that the CN^- is used completely to form products and little free CN^- is present. A set of data consisting of (moles of CN^- consumed)/(moles of complex consumed), from potentiometric and spectral data, gave for 11 samples a value of 3.5 ± 0.1 with no trends with % reaction apparent. If this complex behaves similarly to the two under study, then 3.5 cyanide ions are consumed per complex reacted and the Cu(I) product is $Cu(CN)_3{}^{2-}$... a reasonable formulation.

Summarizing the stoichiometric studies, the reactions may be written as $2Cu(PnAO\text{-}H)^+ + 7\ CN^- + 2OH^- \rightarrow 2Cu(CN)_3{}^{2-} + OCN^- + 1.4PnAO + 1.2CH_3CN$ + fragments and

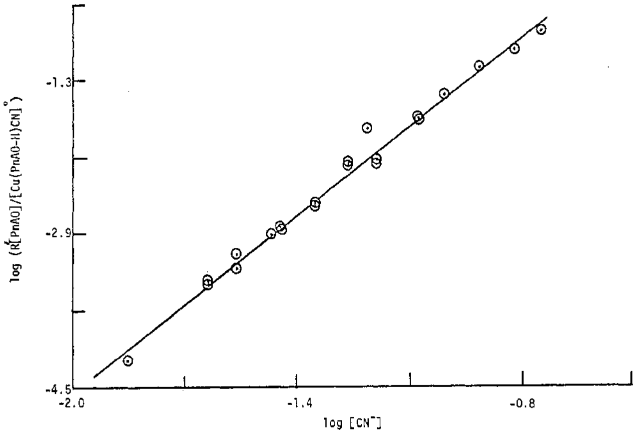


Figure 8. Kinetics of the Cu(PnAO-H)CN^0–CN$^-$ reaction. Rates after 60 s plotted according to eq 5. The line has a slope of 3.0 (pH 12.1, $T = 25$ °C).

2Cu(EnAO-2H)^0 + 7CN$^-$ + 2OH$^-$ → 2Cu(CN)$_3^{2-}$ + OCN$^-$ + 1.2EnAO + 0.8CH$_3$CN + fragments. Further, for each ligand fragmented, two methyl cyanides are formed in the PnAO system and only one in the EnAO analogue. Also, one other component of the fragmentation process was found to be acetone.

Kinetics of Reaction. Since the addition of one CN$^-$ is very rapid, the reactions which were followed were between Cu(AO)CN and excess CN$^-$. The reactions were followed spectrally since only the starting complexes absorbed in the visible region.

Cu(PnAO-H)CN^0–CN$^-$ (580 nm). Preliminary qualitative experiments indicated that the reaction was about first order in complex, a high order in CN$^-$, inversely related to [PnAO], and independent of Cu^{2+}, OCN$^-$, Cu(CN)$_2^-$, or free-radical scavengers added. Since PnAO is generated during the reaction, the reaction did not show first-order kinetic behavior in excess CN$^-$ with the rate diminishing too rapidly. The order with respect to complex was obtained from initial rates. For 13 runs, [CN$^-$] = 0.197 M, $I = 0.64$, pH 12.1, $T = 25.0$ °C, covering the range (0.459–1.835) × 10^{-3} M in complex, the order in complex was found to be 1.04 ± 0.06. Seventeen experiments designed to give the order in CN$^-$ using the initial rates from [complex] = 1.50 × 10^{-3} M, $I = 0.60$, pH 12.1 and over the range (2.33–18.13) × 10^{-2} M CN$^-$ gave a value of 2.03 ± 0.11. Correction was made for the HCN present. It was noted that the rate of reaction abruptly slowed down after about 25–30 s, and this change could not be explained solely by the generation of PnAO. So the order with respect to CN$^-$ was determined later on in the reaction (arbitrarily 60 s). However, since the concentration of PnAO depends on the amount of reaction having taken place, a new expression had to be used. Since the order with respect to PnAO was shown to be −1, the rate at 60 s can be given by

$$R' = \frac{k[\text{complex}][\text{CN}^-]^n}{[\text{PnAO}]} \tag{5}$$

and a graph of log (R'[PnAO]/[complex]) vs. log [CN$^-$] should be linear with a slope of n. The concentration of PnAO was calculated from the known stoichiometry. Figure 8 shows this treatment and clearly gives a slope of 3.02 ± 0.05. Thus, the order in CN$^-$ initially is 2 and changes to 3 later in the reaction.

The order with respect to PnAO was determined by adding free PnAO to the complex solution and adding excess CN$^-$. The slope of the absorption curve at 25% reaction was graphed as a function of [PnAO]$_{\text{free}}$ (both added and produced) and gave a linear relationship. The order with respect to PnAO

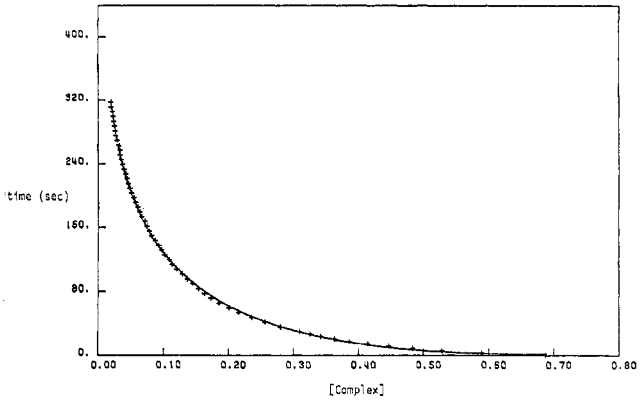


Figure 9. Reaction of Cu(PnAO-H)CN^0 with CN$^-$. The line is a least-squares fit to eq 11. $T = 25$ °C, $I = 0.60$, pH 12.1

at 25% reaction was −0.99 ± 0.01 from 11 data points over the range of (0.1–13) × 10^{-3} M.

An empirical rate expression consistent with these results is

$$\mathrm{d}[\text{complex}]/\mathrm{d}t = \frac{k_a[\text{complex}][\text{CN}^-]^3}{k_b[\text{CN}^-] + k_c[\text{PnAO}]} \tag{6}$$

A mechanism which is consistent with that rate expression is, where [complex] = [Cu(PnAO-H)CN^0]

$$\text{complex} + \text{CN}^- \overset{K}{\rightleftharpoons} \text{complexCN}^- \tag{7}$$

$$\text{complexCN}^- + \text{CN}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cu(CN)}_3^- + \text{PnAO} \tag{8}$$

$$\text{Cu(CN)}_3^- + \text{CN}^- \overset{k_2}{\rightleftharpoons} \text{products} \tag{9}$$

If reaction 7 is very rapid and the steady-state approximation is applied to [Cu(CN)$_3^{2-}$] then it can be shown that

$$k_{\text{obsd}} = \frac{k_1 k_2 K[\text{CN}^-]^3}{k_{-1}[\text{PnAO}] + k_2[\text{CN}^-]} \tag{10}$$

which has the same form as eq 6.

Defining χ as the fraction of reaction generating PnAO, eq 10 can be rearranged to

$$t = \beta_1 + \beta_2 \ln [\text{complex}] + \beta_3[\text{complex}] \tag{11}$$

where

$$\beta_1 = \beta_3[\text{complex}]_0(\ln (\text{complex})_0 - 1) + \ln (\text{complex})_0 K k_1 [\text{CN}^-]^2 \tag{12}$$

$$\beta_2 = -(k_{-1}\chi[\text{complex}]_0 + k_2[\text{CN}^-])/Kk_1k_2[\text{CN}^-]^3 \tag{13}$$

$$\beta_3 = k_{-1}\chi/Kk_1k_2[\text{CN}^-]^3 \tag{14}$$

All complete PnAO runs covering as high as 90% of the reaction were applied to eq 11 using a nonlinear weighted least-squares program. A measure of the fit is given in Figure 9, a representative run, where the line is the calculated least-squares line. For 18 runs β_1, β_2, and β_3 were calculated. Modifying eq 12 gives a linear equation

$$\beta_1[\text{CN}^-]^2 = \beta_3[\text{CN}^-]^2[\text{complex}]_0(\ln (\text{complex})_0 - 1) + \frac{\ln (\text{complex})_0}{Kk_1} \tag{15}$$

to which these set of values can be applied, the results of which are given in Figure 10. From the intercept, Kk_1 can be obtained while the slope is very close to the theoretical value of −0.01116. Combining Kk_1 with eq 14 and assuming a single value of 0.7 for χ (fraction of PnAO recovered) gave a constant value for k_{-1}/k_2 over the entire concentration range studied. Thus, the kinetics of the decomposition of $Cu(PnAO\text{-}H)CN^0$ in excess CN^- follows the rate equation quantitatively over the entire range of reaction in the presence and absence of products.

$Cu(EnAO\text{-}2H)CN^- + CN^-$. The change in absorbance at several wavelengths, principally 575 nm, for this system followed the second-order equation $1/A - 1/A_0 = kt$ over a range of excess $[CN^-]$ ($[CN^-]_T/[complex]_T$ = 80 to 10^4). Addition of free EnAO showed no effect on the second-order rate constant over the range (0–7.2) × 10^{-3}M with $[CN^-]_T$ = 0.090 M and [complex] = 1.1 × 10^{-3} M. Solubility of free EnAO limited studies at higher concentrations. The apparent initial rate was approximately 2 times faster when [EnAO] was 2 × 10^{-4} M or smaller. The presence of $Ni(CN)_4^{2-}$, an EnAO scavenger, at 100 times the molar level of the copper complex did not modify the rate. The order with respect to $[CN^-]$ from the initial slope data is 1.57 ± 0.04 which covers the range 0.1–2.5 M CN^-. While this looks impressive, a graph of k_{obsd} vs. $[CN^-]$ for the second-order rate constants obtained over the entire range of reaction gave a graph of nonzero intercept with a linear portion up to 1 M NaCN, followed by a leveling at 2.5 M NaCN. Since in this system there are spectral changes upon the addition of CN^-, it is believed that the latter behavior represents the true reaction CN^- order for the reaction under study while the initial rate data show a composite having a component of the CN^- association spectral change. Thus, the experimental rate law can be expressed by

$$\frac{-d[\text{complex}]}{dt} = \left[k_a + \frac{k_b[CN^-]}{k_c + [CN^-]}\right][\text{complex}]^2 \qquad (16)$$

Several reasonable mechanisms fit this expression. The one deemed most likely came out of the observation that changes in t_0 absorption intensities occurred upon addition of CN^- suggested an equilibrium of the form

$$Cu(EnAO\text{-}2H)CN^- + CN^- \overset{K_2}{\rightleftharpoons} Cu(EnAO\text{-}2H)(CN)_2^{2-} \qquad (17)$$

The value of this constant, K_2, was estimated by the method of Baker et al.[18] giving 3.6 ± 0.1 M^{-1} and an ϵ of 237 ± 5. A reasonable mechanism would be

$$\text{complex}^- + CN^- \overset{K_2}{\rightleftharpoons} \text{complexCN}^{2-} \qquad (18)$$

$$2\text{complex}^- \overset{k_1}{\rightleftharpoons} \text{products} \qquad (19)$$

$$\text{complex}^- + \text{complexCN}^{2-} \overset{k_2}{\rightleftharpoons} \text{products} \qquad (20)$$

$$2\text{complexCN}^{2-} \overset{k_3}{\rightleftharpoons} \text{products} \qquad (21)$$

where complex$^-$ = $Cu(EnAO\text{-}2H)CN^-$. At low $[CN]^-$, k_{obsd} should follow the equation

$$k_{obsd} = k_1 + k_2K_2[CN]^- \qquad (22)$$

Figure 11 shows such a graph from which the values 0.38 ± 0.23 M^{-1} s^{-1} for k_1 and k_2K_2 = 3.27 ± 0.17 M^{-1} s^{-1} are obtained. At $[CN]^-$ > 0.5 M

$$k_{obsd}[CN]^- = k_2/K_2 + k_3[CN]^- \qquad (23)$$

which is graphed in Figure 11. This gave a value of 6.62 ± 0.40 M^{-1} s^{-1} for k_3. This rationalization appears reasonable since the equilibrium constant is about the expected magnitude and the rate constants increase with increasing CN^- content.

Discussion

The charges on the complexes are +1 for PnAO and 0 for EnAO due to differences in acidity of the intramolecular hydrogen bonds. After the addition of excess CN^- their charges become 0 and −1, respectively (only one CN^- is added). Thus, in neither case is the protonation of the oxime oxygens changed upon association of CN^- in the pH range studied. The question as to whether $Cu(EnAO\text{-}2H)^0$ exists as five-coordinate $Cu(EnAO\text{-}H)(OH)^0$ cannot be settled at present, but on the basis of the Ni(II) case the former is correct. There is, however, a much stronger tendency for five-coordination in the EnAO complex as shown by the fact that the solid perchlorate salt, $[Cu(EnAO\text{-}H)]ClO_4$, exists as a dimer with the oxime O being the bridging group. Also $Cu(EnAO\text{-}H)^+$ has a great attraction for even NO_3^- in aqueous (or more so in CH_3CH_2OH) media.[20] Neither feature is shown by the PnAO complex.

This is also reflected in the $\Delta H°$ values for CN^- association. The EnAO complex is about 6 kcal stronger bonding in spite of the fact that the ionic charges favor the PnAO case. The entropy changes are abnormally high and oppose the enthalpy changes. Thus, at low temperatures the EnAO complex is much more stable toward dissociation while even at room temperature, 20 °C, a factor of 50 exists in favor of the EnAO complex. Most likely this can be attributed to steric hindrance of the apical position in the PnAO complex since both sides of its complex are hindered by the ligand, whereas only one side is hindered with the EnAO complex. The main unexpected feature, however, is the large magnitude of the equilibrium constants and the fact that there is little attraction in either case for the second CN^-.[21] This attests to the strong tendency of Cu(II) to form five-coordinate species with, in this case, a tetragonal-pyramidal structure.

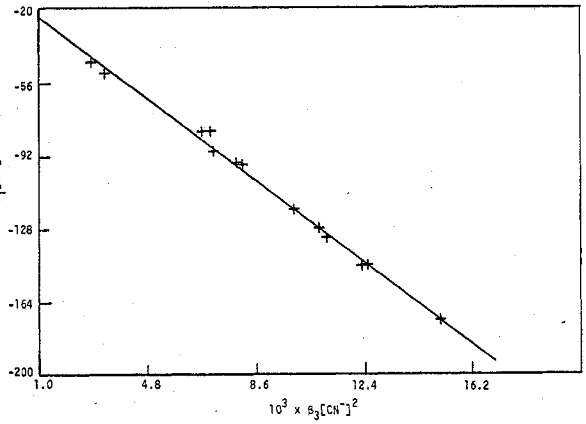


Figure 10. Kinetics of the $Cu(PnAO\text{-}H)CN^0$–CN^- reaction. Least-squares evaluation (line) according to eq 15. T = 25 °C, I = 0.6, pH 12.1.

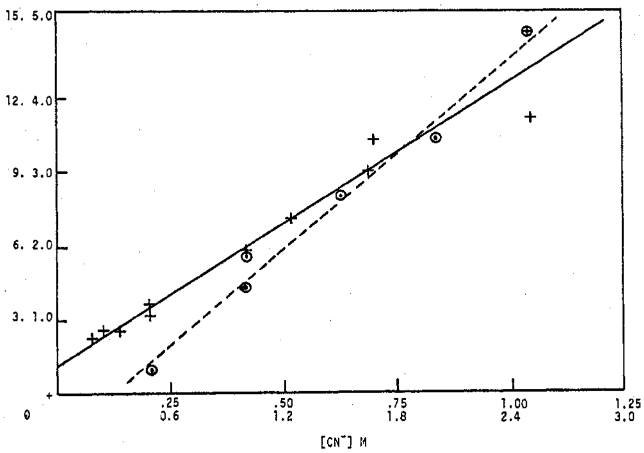
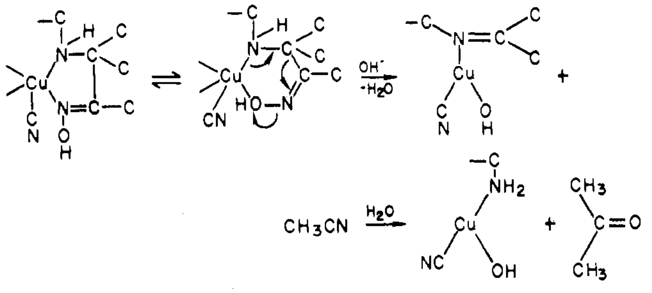


Figure 11. Kinetics of the $Cu(EnAO\text{-}2H)CN^-$–CN^- reaction: (+) low $[CN^-]$ region (eq 22; k_{obsd}, M^{-1} s^{-1}); (O) high $[CN^-]$ region (eq 23; k_{obsd} $[CN^-]$, s^{-1}). T = 25 °C, I = 0.60, pH 12.0.

Over the years, attention has been paid mainly to the rate of loss of Cu(II) or a complex of it in its reaction with CN^- and not to reaction products. The product-study portion of this work has led to some surprising and significant results which have an important bearing on the kinetic expressions and interpretation. The lack of $(CN)_2$ production (often assumed) should have been expected since it reacts so rapidly with basic solutions. However, on the basis of the formation of a yellow polymer by-product which forms whenever $(CN)_2$ reacts with base under the conditions used, $(CN)_2$ is not formed when CN^- reacts with these complexes. The first observable product is OCN^-, which is quantitatively formed. The observation that both PnAO and EnAO fragment during this reaction sequence, but do not unless reacting as a coordinated ligand, is both surprising and may have a far-reaching effect. It remains to be seen if other systems previously studied also involve undetected ligand reaction. The experiments clearly establish that two CH_3CN's are produced from the PnAO complex (not from CN^-) 30% of the time during the CN^- reaction, while only one is found with EnAO. Acetone is also produced as one of the products, but the yield was not established.

In developing a mechanistic pathway for ligand fragmentation which competes with ligand displacement, it seems highly likely that oxime coordination shifts from N to O prior to displacement from the metal ion. The 30% fragmentation which leads to CH_3CN may represent the competition between coordination isomerization and direct dissociation. In the organic sense, the sequence may be pictured

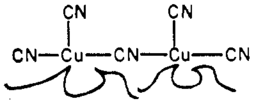


No reasonable explanation is available to explain the 2:1 yield of CH_3CN with the differing ligands.

The portion of the reaction regenerating free PnAO could result from the Cu–amine–N rupture before ligand hydrolysis. In any case, it does not appear necessary or even reasonable to involve oxidation–reduction reactions to explain the products.

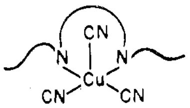
It is not clear at this time as to what effect the ligand fragmentation reaction has on the kinetics. Experimentally, we were not able to measure the PnAO:CH_3CN ratio as a function of fraction of reaction. We were able to show, however, that the total amount of CH_3CN produced was not a major function of reaction rate (as varied with changing CN^-) which suggests that the ratio remains essentially constant throughout the reaction. If the two reactions leading to different products occur before the rate-determining step, then the rate equation should reflect both of the paths and should not conform closely to any relatively simple mechanistic expression. In both cases reported here, close fits to the experimental data with reasonable rate laws were obtained. Thus, it is thought that the fragmentation takes place very close to the activated complex or after it.

The structurally similar complexes react by vastly different rate expressions and with greatly differing rates, EnAO >> PnAO. For the *EnAO complex*, dimerization takes place in the activated complex assisted moderately by CN^-. A tentative picture, consistent with the observations, would involve the formation of a CN^--bridged activated complex by oxime–N dissociation with axial CN^- groups. Electron transfer from a bridged CN^- group to the copper atoms would give OCN^- and relatively labile Cu(I) complexes which would rapidly dissociate. Oxime N–O rearrangement would be a portion of this and would lead to partial fragmentation. The irreversibility of the electron-transfer step would then explain the observed nondependence on free EnAO



A maximum of 2.0 additional CN^-'s could be added in the binuclear activated complex by substitution for the oxime positions.

The fact that the PnAO kinetics are much slower is probably due to steric hindrance to close approach of two metal ion centers. The activated complex could consist of



Again, unwrapping and CN^- coordination seem important. This species, it is postulated, can reversibly dissociate to $Cu(CN)_3^-$ and PnAO. The former, after forming $Cu(CN)_4^{2-}$, could react in a bimolecular fashion[22] and irreversibly go to Cu(I) complexes and OCN^-. Dissociation of the bound ligand into fragments would compete with ligand displacement and give only partial recovery of PnAO.

It is clear that the mechanistic information obtained in this study is somewhat fragmentary, but looking at the basic types of steps for the broad aspects of the reaction it appears that replacement of the oxime–metal bond is necessary, followed either by dimerization, if sterically possible, and then electron transfer or dissociation of amine–metal bonds reversibly and oxidation–reduction between CN^- and cyanide-complexed Cu(II).[23]

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Registry No. CN^-, 57-12-5; $Cu(PnAO\text{-}H)^+$, 66769-06-0; $Cu(EnAO\text{-}2H)^0$, 66769-07-1; $[Cu(PnAO\text{-}H)]ClO_4$, 66769-08-2; $Cu(PnAO\text{-}H)CN^0$, 66769-09-3; $[Cu(EnAO\text{-}H)]ClO_4$, 66769-11-7; $[Cu(EnAO)](ClO_4)_2$, 66769-13-9; $Cu(BnAO\text{-}H)^+$, 66769-14-0; $Cu(EnAO\text{-}2H)CN^-$, 66787-93-7.

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Kinetics and Mechanism of Oxidations by Peroxodiphosphate. 6. Copper(II)-Catalyzed Oxidation of Iodide

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Copper(II)-catalyzed oxidation of iodide with peroxodiphosphate (Perox) has been carried out at $I = 0.5$ M and at 30, 35, 40, and 45 °C. The results conform to the rate law $-d[\text{Perox}]/dt = k_0[\text{Perox}][\text{H}^+] + k_c'[\text{Perox}][\text{Cu}^{\text{II}}]^2[\text{I}^-]/[\text{H}^+]$, where $k_0 = (k_1'[\text{I}^-] + k_2')$. The first term corresponds to the uncatalyzed reaction, and k_c' is a complex rate constant for the catalyzed path. k_0 values (at $[\text{I}^-] = 0.1$ M) were $(7.1 \pm 0.2) \times 10^{-3}$, $(11 \pm 2.2) \times 10^{-3}$, and $(22 \pm 2) \times 10^{-3}$ s^{-1} at 30, 35, and 45 °C, respectively, and compare well with the values found earlier for the uncatalyzed reaction. k_c' values were $(25 \pm 1) \times 10^5$, $(40 \pm 2) \times 10^5$, and $(70 \pm 5) \times 10^5$ $M^{-1}\ s^{-1}$ at 30, 35, and 45 °C, respectively. Copper(II) catalysis operates through complex formation of Cu^{II} with peroxodiphosphate. Moderately concentrated solutions of Cu^{II} and peroxodiphosphate yield a blue precipitate which has these reactants in the ratio 2:1. Spectrophotometric results also suggest complex formation, but there is no kinetics evidence.

The interest in the oxidations by peroxodiphosphate has been of recent origin. Though the oxidation potential of peroxodiphosphate is 2.07 V, it is kinetically inhibited and not much work has been done so far. In most kinetics studies,[1-3] the mechanism involves a rate-determining hydrolytic path. The oxidation[4,5] of iodide is one in which the mechanism is more complicated and also involves a direct reaction between the oxidant and reductant. An iodometric determination[6] of peroxodiphosphate employing copper(II) as catalyst has also been reported. The present paper describes a detailed kinetics study of this catalysis and the mechanism of reaction. The role of copper(II) in peroxodiphosphate oxidations is not yet known and this is perhaps the first reaction in which it has been reported. It would be worthwhile to know whether a Cu^{II}–Cu^{I} cycle operates or whether copper(II) lowers the energy barrier by complex formation with any or both of the reactants. A possibility of both processes is also not ruled out.

Experimental Section

Materials. Tetrapotassium peroxodiphosphate $K_4[P_2O_8]$ was a gift from FMC Corp. Potassium phosphate and potassium flouride present as impurities had no effect on the kinetics of the reaction, and hence the sample was used as such. Its solution was prepared by direct weighing and standardized cerimetrically[7] and iodometrically.[6] The two results were similar. Potassium iodide and copper sulfate were BDH (AnalaR) grade. The perchloric acid was 70% AnalaR Riedel. All other chemicals employed were either BDH (AnalaR) or Merck quality. Doubly distilled water was used for preparing all solutions, the second distillation being from permanganate.

Kinetic Procedure. Iodide, perchloric acid, and other constituents in the desired amounts were taken in a reaction vessel and thermostated at 35 ± 0.1 °C unless otherwise mentioned. A calculated amount of sodium thiosulfate and some starch solution were also added. The reaction was initiated by adding the temperature-equilibrated peroxodiphosphate to the reaction vessel. The iodine liberated reacts with the thiosulfate and the blue color does not appear till the thiosulfate is used up. The time for the appearance of blue color was noted and immediately more of the calculated amount of thiosulfate was added. The process was repeated with decreasing amounts of thiosulfate until 3 half-lives of the reaction were over.

A preliminary study indicated that no reaction occurs between peroxodiphosphate and thiosulfate, if their concentrations are of the same order of magnitude as in the reaction mixture. Similarly starch did not interfere with the kinetics. Small amounts of tetrathionate had no effect on the rate of reaction. No precipitate of cuprous iodide was visible in the reaction mixture. First, the concentration of Cu^{II} employed was small. Second, even if Cu^{I} is formed, it would almost immediately be oxidized by peroxodiphosphate yielding copper(II). A few reactions in acid medium, studied with conventional procedures, showed that if copper(I) and peroxodiphosphate are 1×10^{-3} and 5×10^{-4} M, respectively, the reaction between them is completed in less than the time of rapid mixing, i.e., 2 s at 25 °C. Copper(II) was estimated by noting its absorbance a 710 nm.

Since an equivalent amount of iodide is obtained back from the reaction of iodine and thiosulfate, the concentration of iodide was always constant during a run and the results were pseudo first order for all concentrations of iodide. Hence, pseudo-first-order rate constants were calculated from the straight-line plots of log [Perox] vs. time. The results were reproducible to ±5%.

pH titrations of peroxodiphosphate, with perchloric acid at 35 °C and ionic strength ($LiClO_4$) of 0.5 M, were made on an Expand pH meter from Electronic Corp. of India. These measurements yielded the third and fourth dissociation constants of peroxodiphosphoric acid under the desired conditions.

Spectrophotometric measurements were made on a Beckman DU spectrophotometer using 1-cm cells to determine complex formation between peroxodiphosphate and copper(II) and between iodide and copper(II). A determination of the formation constants was not possible because there is weak complexing and the complexes are not characterized.

A complex of copper(II) and peroxodiphosphate was prepared by mixing concentrated solutions in the absence of any acid. The resulting light blue precipitate was filtered, washed, and dissolved in the least amount of perchloric acid. Copper(II) content was determined iodometrically, and peroxodiphosphate content was determined cerimetrically.

Results

Peroxodiphosphate Dependence. The concentration of peroxodiphosphate was varied in the range $(0.85–42.5) \times 10^{-3}$ M with fixed [KI] = 0.1 M, $[HClO_4]$ = 0.1 M, and $[Cu^{II}] = 1 \times 10^{-5}$ M at 35 °C. In all cases plots of log [Perox] vs. time yielded straight lines. The average value of the pseudo-first-order rate constant (k_{obsd}) was found to be $(17.4 \pm 0.3) \times 10^{-4}$ s^{-1}. These results are given in Table I.

Copper(II) Dependence. The concentration of copper(II) sulfate was varied in the concentration range $(1–50) \times 10^{-6}$

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