Copper(III) Pyrophosphate Complexes in Aqueous Solution. A Pulse Radiolysis Study at Ambient and High Pressure

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The reaction between OH radicals and $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ results in the formation of a Cu(III) complex. No reaction is observed with $N_3^{\bullet}$ or $Br_2^{\bullet -}$, whereas $SO_4^{\bullet -}$ initiates the same steps as seen with $^{\bullet}OH$. This suggests that the mechanism probably involves a ligand interchange or $H^{\bullet}$ atom abstraction process. The Cu(III) complex undergoes a rapid first-order reaction, probably loss of a $P_2O_7^{4-}$ chelate, followed by addition of OH^- ($pK_{OH} \approx 10$) to yield a Cu(III) complex that is predominantly hydroxylated and has a relatively long half life. The effect of pressure (up to 150 MPa) on the formation and subsequent reactions of the Cu(III) complex is used to help elucidate the mechanism of the different steps.

Introduction

Cu(III) has an extensively studied coordination chemistry and has been implicated as an intermediate in both enzymatic and nonenzymatic reactions in various systems.[1] Peptide complexes of Cu(III) are remarkably stable in neutral aqueous solution. In general they undergo acid- and base-catalyzed redox decomposition reactions in which various protonated, dechelated, and deprotonated forms are the redox active species.[2,3] Evidence for a decarboxylation reaction prior to the redox decomposition has been reported.[4] These findings all underline the remarkable substitution stability of Cu(III) complexes in such systems, as compared to the very labile complexes usually formed by Cu(II).

Pulse radiolysis studies of the oxidation of copper ions and hydroxo complexes by OH radicals in acidic to almost neutral pH have shown that transient Cu(III) complexes are formed.[5,6] In addition, the equilibrium between $Cu(OH)_2^+$ and $Cu(OH)_3$ was established.[5,7] These studies suggest that the $Cu(OH)_3$ complex is formed at neutral pH at a rate of $k_1 = 3 \times 10^8$ M^{-1} s^{-1} and is in equilibrium with the $Cu(OH)_2^+$ species with a pK_2 of 4.0.

$$Cu^{2+} + {}^{\bullet}OH + 2H_2O \rightarrow Cu(OH)_3 + 2H^+ \quad k_1 \qquad (1)$$

$$Cu(OH)_3 + H^+ \rightleftarrows Cu(OH)_2^+ + H_2O \quad K_2 \qquad (2,-2)$$

Studies at pH 6 have shown that there is no change in k_1 as a function of pressure and suggest that the system is best described by a rate-determining ligand−interchange mechanism.[8] The mechanism by which $Cu(OH)_2^+$ and $Cu(OH)_3$ disappear involves the formation of peroxide and, at lower pH, the probable formation of an OH radical.[6] These earlier studies were limited to the pH range of 0−7 because of the formation of insoluble copper oxides at higher pH. The only other experimental “window” in aqueous solution is at very alkaline pH, where the copper is made soluble by the addition of high concentrations of OH^-.

Pyrophosphate ($P_2O_7^{4-}$) is a very good ligand for the formation of Cu(II) complexes at neutral and alkaline pH. It has been established[9,10] that, between pH 7−10, the predominant species in solution is a Cu(II) complex with two $P_2O_7^{4-}$ ligands. Recent ^{31}P and ^{1}H NMR studies[11] have shown that the complex in this pH range is $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$. The complex is most probably six coordinate, with the $P_2O_7^{4-}$ serving as a bidentate chelate and each phosphorus having a tetrahedral geometry. A crucial feature for pulse radiolysis experiments is that $P_2O_7^{4-}$ reacts relatively slowly with OH radicals, making it possible to oxidize the Cu(II) complex without interference of competitive ligand oxidation.[12,13]

Our aim in this paper is to generate and characterize Cu(III) complexes in aqueous solution in neutral to alkaline pH. Then, having established the conditions under which a reasonably stable Cu(III) complex is formed and the nature of the complex, it may be possible to probe the reactivity of that complex with other metal complexes or with organic substrates. In order to assist the elucidation of the underlying reaction mechanisms, we have also studied the effect of high pressure on the formation of the various Cu(III) complexes.[14−16]

Materials and Methods

Materials. All solutions were prepared using water that, after distillation, was passed through a Millipore ultrapurification unit. Copper(II) pyrophosphate solutions were prepared by mixing $Na_4P_2O_7{\cdot}10H_2O$ (Alfa Products) and $CuSO_4$ (puratronic, Johnson Matthey Chemicals, Ltd.). The pH was adjusted by the addition of sodium hydroxide or sulfuric acid (both Ultrex, J. T. Baker Chemical Co.). The ionic strength was fixed when necessary by the addition of $NaClO_4{\cdot}H_2O$ (G. F. S. Chemicals). The *t*-BuOH (Aldrich Chem. Co.) was purified by successive recrystallization. NaN_3, $Na_2S_2O_8$, and KBr were of the highest purity commercially available and used as is. Hydrogen peroxide was Ultrex (J. T. Baker Chemical Co.) and all gases used (N_2O and O_2) were UHP grade (99.999% purity).

Methods. The pulse radiolysis experiments were carried out at the Brookhaven National Laboratory 2 MeV van de Graaff accelerator. Dosimetry was carried out using 10 mM KSCN and taking the molar extinction coefficient of $(SCN)_2^-$ as 7950 M^{-1} cm^{-1} at 472 nm, assuming a G value of 6.13. The path length was 2 cm, and the dose was varied from 0.5−20 μM

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radical. Experimental conditions were 25 °C and ambient pressure unless otherwise specified. ^{60}Co γ-ray experiments were carried out in a source that emits 400 rad/min. All UV−vis data were collected on a Cary 210 spectrophotometer thermostated to 25 °C.

All experiments were carried out using at least a 4:1 excess of pyrophosphate. The quoted molar extinction coefficients were obtained assuming a G value of 5.3 unless otherwise specified (as calculated using the equation given in ref 24) and that complete scavenging of the primary radicals occurred. No changes in the UV−vis absorbance of the Cu(II)pyrophosphate solution was observed between pH 7 and 11.5. Pulse radiolysis experiments at elevated pressure (up to 150 MPa) were performed in a four-window high-pressure cell using a pillbox optical cell as described elsewhere.[4,17,18]

Results

Upon radiolysis of water, the following species are formed:[19]

$$H_2O \rightsquigarrow OH(2.74),\ e_{aq}^-\ (2.76),\ H(0.55),\ H_2O_2(0.72),\ H_2(0.45) \quad (I)$$

The values in parentheses are G values, that is, the number of species produced per 100 eV of energy dissipated in water. Irradiation of an N_2O saturated (0.022 M) aqueous solution results in the conversion of e_{aq}^- to OH radicals, reaction 3 with a rate constant of $k_3 = 9 \times 10^9$ M^{-1} s^{-1}.[20]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + {}^{\bullet}OH + OH^- \quad k_3 \qquad (3)$$

If N_3^- or Br^- is added to the above solution, the $^{\bullet}$OH radical is scavenged to yield the oxidizing radicals $N_3^{\bullet}$ or $Br_2^{\bullet -}$ with a rate constant[20] of $k_4 = 1.2 \times 10^{10}$ M^{-1} s^{-1} and $k_5 = 1.1 \times 10^{10}$ M^{-1} s^{-1}.

$${}^{\bullet}OH + N_3^- \rightarrow N_3^{\bullet} + OH^- \quad k_4 \qquad (4)$$

$${}^{\bullet}OH + Br^- \rightarrow {}^{\bullet}BrOH^- \quad k_5 \qquad (5)$$

$${}^{\bullet}BrOH^- + Br^- \rightarrow Br_2^{\bullet -} + OH^- \quad k_6 \qquad (6)$$

The oxidizing radical $SO_4^{\bullet -}$ is generated in an argon saturated solution containing peroxodisulfate with a rate constant of $k_7 = 1.2 \times 10^{10}$ M^{-1} s^{-1}. The e_{aq}^- can also reduce $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$. The rate of reaction 8 was measured to establish the concentration range where N_2O scavenging

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad k_7 \qquad (7)$$

$$[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-} + e_{aq}^- \rightarrow [Cu^{I}(P_2O_7)_2(H_2O)_2]^{7-} \quad k_8 \qquad (8)$$

of the aqueous electron will dominate. *tert*-Butanol is an effective $^{\bullet}$OH radical scavenger; the resultant *tert*-butyl radical is relatively unreactive but, at most, it will reduce $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ or add on to the metal.[21] Reaction 8 was monitored by following the disappearance of e_{aq}^- at 700 nm (10 mM *tert*-butanol, 50− 200 μM $CuSO_4$, 1 mM pyrophosphate, pH 11.0); $k_8 = 1.3 \times 10^9$ M^{-1} s^{-1}. The slow rate constant for reaction 8 relative to reaction 3 allows N_2O scavenging to dominate even at 10 mM $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$.

The H atom, although formed with a relatively small yield, is known to reduce Cu_{aq}^{2+} ions ($k_9 \leq 9.1 \times 10^7$ M^{-1} s^{-1} [20]). At high pH, the H atom is converted to the e_{aq}^- via reaction 10, with

$$H^{\bullet} + Cu_{aq}^{2+} \rightarrow Cu_{aq}^{+} + H^+ \quad k_9 \qquad (9)$$

$$H^{\bullet} + OH^- \rightarrow e_{aq}^- + H_2O \quad K_{10} \qquad (10,-10)$$

p$K_{10} = 9.6$ ($k_{10} = 2.4 \times 10^7$ M^{-1} s^{-1} [22] and $k_{-10} = 1000$ s^{-1} [23]). The rate of reaction between $H^{\bullet}$ and $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ was not measured but the results suggest that the reaction occurs with a rate constant that is somewhat lower than k_9 (vide infra).

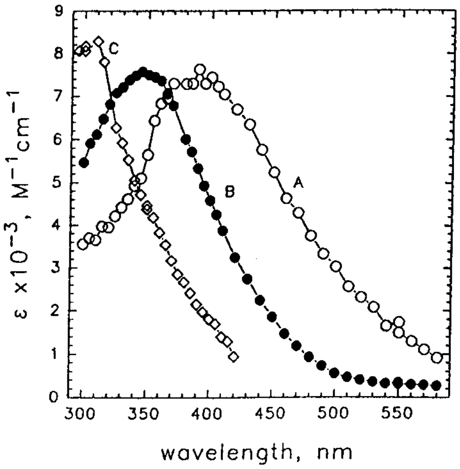

Figure 1. The molar absorbances as a function of wavelength for the transients formed at (A) 2 μs, (B) 30 μs, (C) 5 ms. Conditions: pH 11.0, 5 mM $[Cu(P_2O_7)_2(H_2O)_2]^{6-}$, 15 mM $P_2O_7^{4-}$, N_2O saturated, 0.5 M $NaClO_4$.

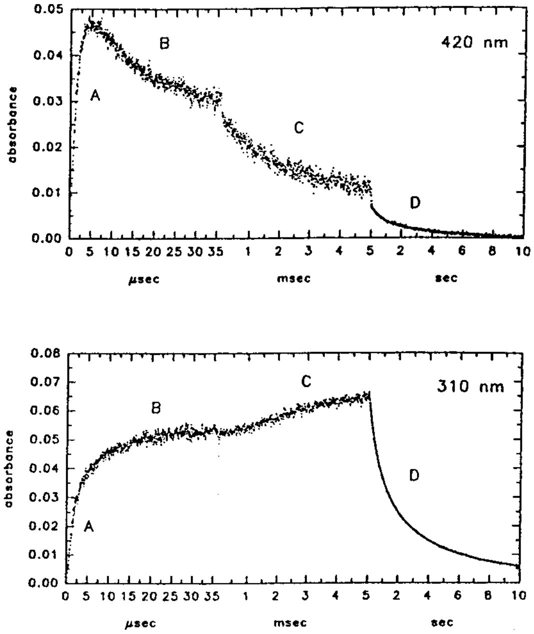

Figure 2. The change in absorbance as a function of time for pulse radiolysis traces at 35 μs, 5 ms and 10 s (420 and 300 nm) showing the formation of transients **A**, **B**, and **C** and the disappearance of transient **C** (D). Conditions: pH 11.0, 5 mM $[Cu(P_2O_7)_2(H_2O)_2]^{6-}$, 25 mM $P_2O_7^{4-}$, N_2O saturated.

The molar extinction coefficients that are quoted in this paper were obtained using G values calculated from the equation of Schuler et al.[24] using a $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ concentration of 0.5−10 mM. At pH < 11, where the H atom is not converted to the hydrated electron, the G(OH) was taken as 5.2−5.33. At pH > 11, where $H^{\bullet}$ is effectively converted to hydrated electrons and then to OH radicals via addition of N_2O, the G(OH) was taken as 5.8−5.93.

Upon pulse radiolysis of a N_2O-saturated aqueous solution containing 0.005−0.2 M pyrophosphate and 0.001−0.02 M $CuSO_4$, a transient is formed with a maximum at 400 nm and a molar absorbance of 7400 M^{-1} cm^{-1}, Figures 1A and 2A (top and bottom trace). Since $k(^\bullet OH + P_2O_7^{4-}) = 2.2 \times 10^5$ M^{-1} s^{-1} at pH 10.0, a ratio of $[P_2O_7^{4-}]/[Cu^{II}(P_2O_7)_2(H_2O)_2^{6-}] < 15/1$ was maintained in order to insure that the $^\bullet$OH did not react directly with $P_2O_7^{4-}$.

The rate of this initial reaction varies with copper complex concentration and plots of k_{obs} vs $[Cu^{II}(P_2O_7)_2(H_2O)_2^{6-}]$ at pH 8 and pH 11 yield straight lines with small intercepts, for which $k_A = 9.3 \times 10^7$ M^{-1} s^{-1}, Figure 3. The intercepts ((1−2) × 10^5 s^{-1}) are larger than expected from $^\bullet$OH recombination (k[OH] ~ (1−4) × 10^4 s^{-1}) or reaction of $^\bullet$OH with $P_2O_7^{4-}$ ($k[P_2O_7^{4-}] \sim 2 \times 10^4$ s^{-1}). It is possible that much of the intercept is due to the reversibility of one of the steps forming transient **A** (see Scheme 1).

SCHEME 1

$$Cu^{II}(P_2O_7)_2(H_2O)_2^{6-} + {}^\bullet OH \xrightarrow{k_A} [Cu^{II}(P_2O_7)_2(H_2O)(OH)]^{6-} + H_2O \quad (A)$$

$$[Cu^{II}(P_2O_7)_2(H_2O)(OH)]^{6-} \xrightarrow{\text{fast}} \underset{\mathbf{A}}{[Cu^{III}(P_2O_7)_2(H_2O)(OH^-)]^{6-}}$$

$$[Cu^{III}(P_2O_7)_2(H_2O)(OH^-)]^{6-} \xrightarrow{k_B} \underset{\mathbf{B}}{[Cu^{III}(P_2O_7)_2(H_2O)(OH^-)]^{2-}} + P_2O_7^{4-} \quad (B)$$

$$\underset{\mathbf{B}}{[Cu^{III}(P_2O_7)(H_2O)(OH^-)]^{2-}} + OH^- \overset{K_c}{\rightleftharpoons} \underset{\mathbf{C}}{[Cu^{III}(P_2O_7)(H_2O)(OH^-)_2]^{3-}} \quad (C,-C)$$

$$\underset{\mathbf{B}\text{ or }\mathbf{C}}{2[Cu^{III}(P_2O_7)(H_2O)(OH^-)]^{2-}} \xrightarrow[2P_2O_7^{4-}]{k_D} 2\,Cu^{II}(P_2O_7)_2(H_2O)_2^{6-} + H_2O_2 \quad (D)$$

$$\underset{\mathbf{B}}{[Cu^{III}(P_2O_7)(H_2O)(OH^-)]^{2-}} + H_2O_2 \xrightarrow[P_2O_7^{4-}]{k_E} Cu^{II}(P_2O_7)_2(H_2O)_2^{6-} + HO_2 \quad (E)$$

$$\underset{\mathbf{B}}{[Cu^{III}(P_2O_7)(H_2O)(OH^-)]^{2-}} + HO_2 \xrightarrow[P_2O_7^{4-}]{k_F} Cu^{II}(P_2O_7)_2(H_2O)_2^{6-} + O_2 \quad (F)$$

$$\underset{\mathbf{C}}{[Cu^{III}(P_2O_7)(H_2O)(OH^-)_2]^{3-}} + H_2O_2 \xrightarrow[P_2O_7^{4-}]{k_G} Cu^{II}(P_2O_7)_2(H_2O)_2^{6-} + O_2 \quad (G)$$

The initial transient disappears at a first-order observed rate of (7−8) × 10^4 s^{-1} (Figure 2B) with the concomitant formation of a transient with a maximum at 350 nm and a molar absorbance of ≈7600 M^{-1} cm^{-1}, Figure 1B. This rate constant is independent of ionic strength, $[P_2O_7^{4-}]$, [Cu(II)], and dose. A very small decrease in rate with pH is observed; at low pH (ca. 7−8), the rate decreases to (2−4) × 10^4 s^{-1}.

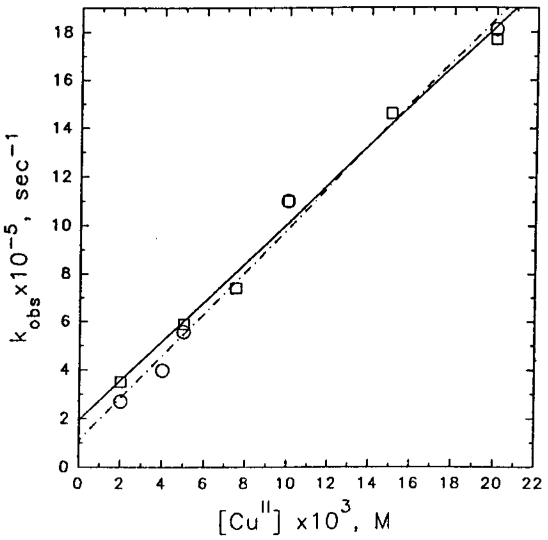

Figure 3. The change in observed rate as a function of $[Cu(P_2O_7)_2(H_2O)_2]^{6-}$ for reaction A. Conditions: 0.05−0.2 M $P_2O_7^{4-}$, N_2O saturated, pH 8 (○) and 11 (□).

At pH < 9.5, a first-order disappearance of roughly 10% of transient B is observed. This rate is proportional to the concentration of transient B in solution, yielding a bimolecular rate constant of (2−3) × 10^8 M^{-1} s^{-1}. This process is likely a reaction between the Cu(III) complex and the Cu^I formed by reduction of $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ by $H^\bullet$. At high pH (pH ≥ 11), this first-order process is no longer observed. As a competition exists between OH^- and $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ for $H^\bullet$ at pH 11, reaction 10 is preferentially removing the H atom.

To confirm this mechanism, an argon-saturated aqueous solution containing 0.2 M pyrophosphate and 0.01−0.04 M Cu(II) at pH 8.5 was pulse irradiated. Here, both e_{aq}^- and $H^\bullet$ reduce $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$. A bimolecular rate constant for the reaction of Cu(III) and Cu(I) of 3.4 × 10^8 M^{-1} s^{-1} was calculated using the kinetic equation describing A + B → C where $[\mathbf{A}] \neq [\mathbf{B}]$ and assuming that [Cu(I)] = 1.2 [Cu(III)].[19]

At pH > 9.5, transient **B** disappears by a strictly first-order process with the concomitant formation of a third transient with a maximum at 300 nm and a molar absorbance of ≈8500 M^{-1} cm^{-1}, Figures 1C and 2C. The rate of this process is independent of dose and $[[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}]$ and appears to be relatively independent of $[P_2O_7^{4-}]$. The rate is, however, proportional to $[OH^-]$ and is strongly ionic strength dependent, Figure 4. As shown in Figure 4, k_c, k_{-c}, and K_c are 8.3 × 10^6 M^{-1} s^{-1}, 1.4 × 10^3 s^{-1}, and 5.8 × 10^3 M^{-1}, respectively, when measured in a solution containing both 0.5 M $NaClO_4$ and 0.05 M pyrophosphate. These rate constants all become slower at lower ionic strength; the traces in Figure 2 were measured at significantly lower ionic strength. However, it is impossible to quantify the ionic strength effect and thus obtain a measure of the charge on transient **B** since the overall ionic strength of the solution is so high.

Both Cu(III) complexes (**B** and **C**) disappear by processes that display mixed kinetics but are predominantly bimolecular. The rate constants associated with these processes are of the order of $k_D \sim 10^5$ M^{-1} s^{-1}. As both Fe(IV) pyrophosphate[12] and Cu_{aq}^{3+} [6] decay by second-order processes with the formation of peroxide (with, in the latter case, an additional pathway that is first order and forms OH radicals[6]), a mechanism involving reaction D in Scheme 1 seems likely. In order to further define the mechanism, the reactions between both Cu(III) forms **B** and **C** were studied as a function of peroxide concentration, reactions E and G in Scheme 1. Both reactions were shown to occur

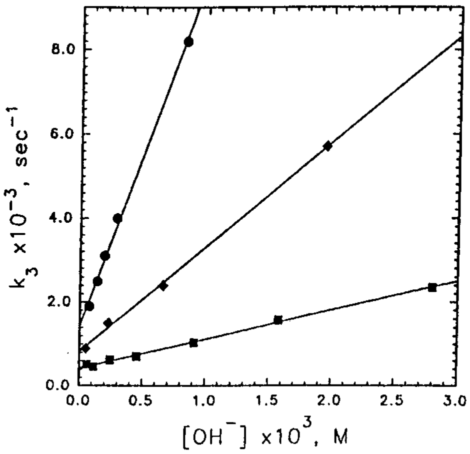

Figure 4. The change in observed rate as a function of [OH$^-$] for reaction C. Conditions: N_2O-saturated aqueous solutions containing (●) 0.5 M $NaClO_4$, 0.05 M $P_2O_7^{4-}$, 0.01 M $CuSO_4$ (◆) 0.67 M $NaClO_4$, 0.013 M $P_2O_7^{4-}$, 2 mM $CuSO_4$; (■) 0.1 M $NaClO_4$, 0.01 M $P_2O_7^{4-}$, 2 mM $CuSO_4$

with rate constants of $k_E = 7.3 \times 10^5$ M^{-1} s^{-1} and $k_G \sim 2.4 \times 10^6$ M^{-1} s^{-1}. Both of these reactions yield HO_2 radicals, which at pH 7 will rapidly deprotonate to yield O_2^-. Therefore, an O_2-saturated solution containing $CuSO_4$ (2−10 mM) and $P_2O_7^{4-}$ (0.1 M) was pulse irradiated. Here, the e_{aq}^- adds to O_2 to yield O_2^- while the OH radical reacts with the Cu(II) complex to yield, ultimately, either **B** or **C**. The rate constant for the reaction between O_2^- and **B** or **C** was measured under second-order conditions; $k_F = 2 \times 10^8$ M^{-1} s^{-1}. As is apparent, all of these reactions are as fast or faster than k_D and will, therefore, enter into the overall mechanism. The extent to which the observed kinetics can be fitted by these four reactions and whether OH radicals are indeed formed or a first-order process involving ligand decomposition occurs are out of the scope of this paper. No formation of a final product absorbance in the UV−vis or net loss of $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ was observed on the time scale of these experiments (from 1 μs to 100 s).

The net recovery of all the parent $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ complex in the overall mechanism was confirmed by ^{60}Co γ-ray studies. Irradiation of a N_2O-saturated solution at pH 11 led to no loss of starting $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ and no formation of either a precipitate or of metallic copper.

The three processes observed at pH 11.0 were measured as a function of temperature, Figure 5. The log k_{obs} values were, in all cases, linear with the change in temperature (15−83 °C) and activation parameters were obtained, Table 1. In addition, the three aforementioned processes were also studied at pH 11.0 as a function of pressure, Figure 6. The ln k_{obs} vs pressure plots were linear over the pressure range 4.8−148 MPa, and activation volumes were calculated from the slopes ($-\Delta V^{\#}/RT$) of these plots.

$Br_2^{\bullet -}/N_3^{\bullet}$ were generated by pulsing N_2O-saturated aqueous solutions containing either 0.1 M KBr or 0.1 M NaN_3 and 0.1 M $P_2O_7^{4-}$ and 0.01 M $CuSO_4$ at pH 10. No reaction was observed at 0.4 μM $Br_2^{\bullet -}$, yielding a limiting rate of $k(Br_2^{\bullet -} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}) < 1 \times 10^5$ M^{-1} s^{-1}. No reaction was observed with 0.4 μM $N_3^{\bullet}$, giving a limiting rate of $k(N_3^{\bullet} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}) < 2.7 \times 10^5$ M^{-1} s^{-1}. $SO_4^{\bullet -}$ was generated by pulse irradiating an Ar-saturated aqueous solution containing 0.1 M $P_2O_7^{4-}$, 0.1 M $Na_2S_2O_8$, and 0.01 M $CuSO_4$ at pH 10.5. A rate constant of $k(SO_4^{\bullet -} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}) = 1.4 \times 10^7$ M^{-1} s^{-1} was measured. More significantly, the subsequent processes described above for the $^{\bullet}$OH initiated mechanism were also observed here.

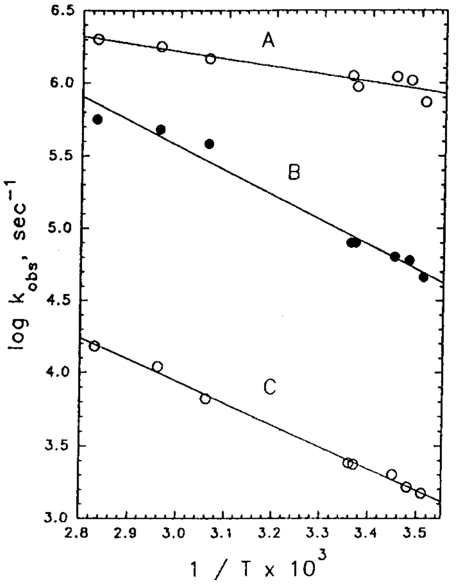

Figure 5. Arrhenius plots of the three observed processes at pH 11.0. Conditions: 0.05 M $P_2O_7^{4-}$, 7.5 mM $CuSO_4$, N_2O saturated.

TABLE 1: Summary of the Measured Activation Parameters

	E_a, kJ/mol	A	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/(mol K)	$\Delta V^{\ddagger}$, cm^3/mol
A	10.2 ± 1.5	6.2×10^{10}	7.5 ± 1.5	−66 ± 5	−1.8 ± 0.7
B	33.0 ± 2.1	5×10^{10}	30.4 ± 2.1	−48 ± 7	−2.4 ± 0.3
C	28.9 ± 0.8	2.7×10^8	26.3 ± 0.8	−92 ± 3	−5.6 ± 0.4

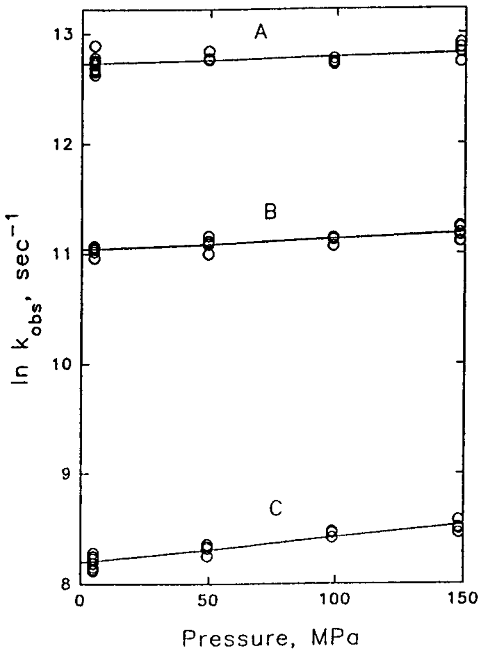

Figure 6. The change in rate as a function of pressure for the three observed processes at pH 11.0. Conditions: 0.05 M $P_2O_7^{4-}$, 7.5 mM $CuSO_4$, N_2O saturated.

Discussion

The observed processes can be described by the mechanism given in the Scheme 1. A limited number of studies have been reported in which the metal center of Cu(II) complexes have been oxidized by inorganic radicals; see Table 2 for a selection of relevant rate constants (ref 20 and references cited therein). The rates, taken in conjunction with the redox potentials for these radicals ($E^0(^{\bullet}OH/OH^-) = 1.89$ V, $E^0(^{\bullet}OH,H^+/H_2O) = 2.74$ V, $E^0(SO_4^{\bullet -}/SO_4^{2-}) = 2.43$ V, $E^0(Br_2^{\bullet -}/2Br^-) = 1.66$ V, $E^0(N_3^{\bullet}/$

TABLE 2: Summary of Relevant Reactions of Copper Complexes

reaction	k, $M^{-1}\,s^{-1}$	$\Delta V^{\ddagger}$, $cm^3\,mol^{-1}$	ref
$^{\bullet}OH + Cu_{aq}{}^{2+} \rightarrow Cu_{aq}{}^{3+} + OH^-$	3.5×10^8	0.7	7
$N_3{}^{\bullet} + Cu^{II}$GlyGlyHis $\rightarrow Cu^{III}$GlyGlyHis $+ N_3{}^-$	5×10^8	5	4
$^{\bullet}Br_2{}^- + Cu^{II}$GlyGlyHis $\rightarrow Cu^{III}$GlyGlyHis $+ 2Br^-$	4×10^7		4
$^{\bullet}OH + [Cu^{II}\,(P_2O_7)_2(H_2O)_2]^{6-} \rightarrow [Cu^{III}(P_2O_7)(H_2O)_2]^{5-} + OH^-$	9×10^7	−1.8	this work
$SO_4{}^{\bullet -} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-} \rightarrow [Cu^{III}(P_2O_7)_2(H_2O)_2]^{5-} + SO_4{}^{2-}$	1×10^7		this work
$Br_2{}^{\bullet -} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-} \rightarrow$ nr[a]	$<1 \times 10^5$		this work
$N_3{}^{\bullet} + [Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-} \rightarrow$ nr[a]	$<2.7 \times 10^5$		this work

[a] nr = no reaction.

$N_3{}^-) = 1.33$ V)[25], suggest that the initial process described here is best described as a rate-determining ligand-interchange reaction.[26] In addition, the oxidation potential for $SO_4{}^{\bullet -}$ is, at pH 8−11, considerably higher than that of $^{\bullet}OH$, while the rate of oxidation of the copper complex by the former is slower. This argues against an outer sphere electron transfer process as observed upon oxidation of Cu^{II}GlyGlyHis by $N_3{}^{\bullet}$. The relatively low measured activation energy for the reaction A is also in accord with this mechanism.

Strong support for this mechanism comes from the very small activation volume found for the first step (reaction A, Scheme 1). The value of -1.8 ± 0.7 $cm^3\,mol^{-1}$ is very small and in close agreement with that found for the reaction of $Cu^{2+}{}_{aq}$ with $^{\bullet}OH$ [8]. Furthermore, it was recently reported that electron transfer reactions between metal ions and radicals that are not diffusion controlled exhibit pressure dependences that support a ligand-substitution controlled process.[25] Ligand substitution on aquated Cu(II) ions is expected to follow a dissociative interchange mechanism (I_d) due to Jahn−Teller distortion.[27] However, in the case of chelating Cu(II) complexes a changeover to an associative interchange mechanism (I_a) can occur, as was recently reported for solvent exchange and complex formation reactions of $Cu(tren)H_2O^{2+}$ (tren = 2,2′,2″-triaminotriethylamine).[28] The slightly negative volume of activation found in the present system can therefore be interpretated as evidence for a pure interchange (I) or an associative interchange (I_a) mechanism that controls the interaction between $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ and $^{\bullet}OH$.

The second process (reaction B, Scheme 1) is accompanied by a significant blue shift of the absorption spectrum, a substantively higher activation energy, and a slightly more negative volume of activation. While we recognize that the affinity of Cu(III) for pyrophosphate might be expected to be greater than that of Cu(II), these observations are interpreted as evidence for the loss of $P_2O_7{}^{4-}$ on the Cu(III) transient. In general, complexation of copper by $P_2O_7{}^{4-}$ is accompanied by a red shift in the absorption spectrum, viz. $Cu^{2+}{}_{aq}$ (220 nm) vs $[Cu^{II}(P_2O_7)_2(H_2O)_2]^{6-}$ (270 nm) and $Cu(OH)_3/Cu(OH)_2{}^{+}$ (300 nm) vs $[Cu^{III}(P_2O_7)_2(H_2O)_2]^{5-}$ (400 nm). Thus the observed blue shift (Figure 1) could be indicative of the loss of $P_2O_7{}^{4-}$. This reaction exhibits no significant pH dependence, i.e., does not involve a reaction with OH^- and most probably involves the rate-determining ring-opening of the $P_2O_7{}^{4-}$ chelate. Such a ring-opening reaction will involve some charge separation that can compensate the expected intrinsic volume increase and result in the observed overall negative volume of activation of -2.4 ± 0.3 $cm^3\,mol^{-1}$. Alternatively, dechelation can involve rate-determining binding of a solvent molecule in an interchange fashion, *i.e.*, the entrance of a solvent molecule into the Cu(III) coordination sphere accompanied by ring opening of the chelate. Such a process could easily result in the small negative volume of activation.

The third step (reaction C, Scheme), that occurs at high pH, has a rate that exhibits an OH^- dependence and increases with ionic strength, suggesting a reaction between two negative species. This is likely the addition of hydroxide as a ligand to the copper accompanied by the partial loss of pyrophosphate. This could involve the loss of $P_2O_7{}^{4-}$ from the ring-opened transient produced in the second reaction step or from the remaining chelate on the Cu(III) center. Transient **C** bears strong resemblance spectrally to all of the Cu^{III} hydroxides that are known.[6] At lower pH, this reaction is not observed because of the equilibrium with a back reaction that involves binding of $P_2O_7{}^{4-}$. In general, Cu(II) hydroxo species are expected to be significantly less labile than the corresponding aqua species, which will account for the absence of the back reaction in basic medium. The volume of activation found for the third process, -5.6 ± 0.4 $cm^3\,mol^{-1}$, is significantly more negative than for the first two reaction steps. The coordination of an additional hydroxy ligand will be accompanied by a volume collapse due to a small contribution from intrinsic effects and a larger contribution due to solvational effects as a result of charge concentration.

Again the binding of OH^- could follow an I_a type of mechanism if it involves the simultaneous or concerted release of coordinated $P_2O_7{}^{4-}$. Such an interchange process will also account for the observed activation volume.

If we compare the activation entropies and volumes for all three reactions, we can see an interesting trend. Going from reaction A to B we can observe a decrease in the activation entropy from −66 to −91.6 J/K mol. This decrease is in line with the decrease in the activation volume from −1.8 to −5.6 cm^3/mol, indicating a direct connection between both parameters.

Studies are currently in progress that address the issues of Cu(III) reactivity with other metal complexes and organic compounds and the mechanism of decay of the final Cu(III) transient(s) over a pH range of 8−11.5 as mentioned above.

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