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Kinetics and Mechanism of the Reaction of Copper(II) with Hydroxylamine in the Presence of Bathocuproine Disulfonate

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Synopsis. The stoichiometry and the mechanism of the electron-transfer reaction of Cu(II) with hydroxylamine are investigated by measuring a fast complex formation of Cu(II) with bathocuproine disulfonate. The data are evaluated for the rate-determining step involving a radical species.

Hydroxylamine acts as a reducing agent on various metal ions,[1] the stoichiometry of the reaction being dependent on the metal species and on the acid concentration of the medium.[2]

Bathocuproine disulfonate (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline disulfonate; abbr. BCDS) was used as a specific chelating agent for copper(I) forming a very stable complex of intense color.[3] The corresponding complex of the bivalent copper has not been reported owing to its low stability due to the steric hindrance of the ortho-methyl groups of the ligands in the square planar complex.

We report here the stoichiometry and the kinetics of the reaction between copper(II) and hydroxylamine. The copper(I) formed in the reaction was measured by stopped-flow method as a colored 1 : 2 complex of BCDS. The very fast complex formation of univalent copper ion was found to be useful as an indication of the slow redox reaction.

Experimental

Reagents. Reagent grade chemicals were used. The stock solution of copper(II) sulfate (Koso) was titrated with EDTA. Hydroxylammonium sulfate (Wako) was dissolved in distilled water free from oxygen, and stored in a refrigerator under nitrogen atmosphere. The concentration of the stock solution was determined with potassium permanganate. Disodium bathocuproine disulfonate (Dojindo) was dissolved in water to prepare a 1.00×10^{-3} M stock solution.[4] The ionic strength was adjusted at 0.15 with potassium sulfate (Koso).

Stoichiometry. The composition of the complex species was confirmed using the absorption peak of the copper(I)-BCDS complex at 483 nm ($\varepsilon_{\max}=1.27\times10^4$). The stoichiometry of the reaction of copper(II) with hydroxylamine was also determined spectrophotometrically at 483 nm.

Kinetics. The reaction of copper(II) with hydroxylamine was followed spectrophotometrically at 483 nm using a Yanagimoto SPS-1 stopped-flow apparatus. Reservoirs of the reagent solutions were kept under nitrogen atmosphere to avoid air oxidation. Kinetics was studied in the acid region under the condition $[NH_2OH]_0 \gg [BCDS]_0 > [Cu(II)]_0$, $\mu=0.15$ (K_2SO_4), and at 25.0±0.2 °C.

Results and Discussion

Stoichiometry. The parent compound bathocuproine (4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline) has been known to form a 1 : 2 complex with copper(I). We confirmed by the mole ratio method that the BCDS also forms a 1 : 2 complex with copper(I) as shown in Fig. 1.

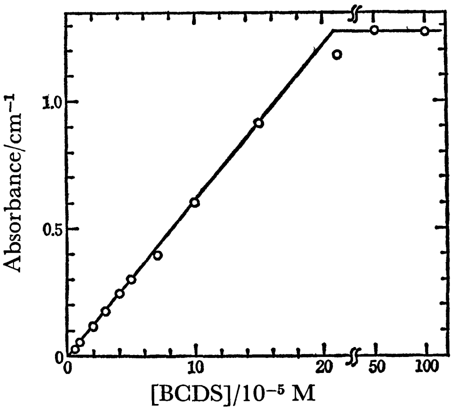

Fig. 1. Mole ratio method for the formation of Cu(I)-BCDS complex.
$[Cu(II)]_0=1.008\times10^{-4}$ M, $[NH_2OH]_0=1.23\times10^{-2}$ M, pH=4.0 (acetate buffer), $\mu=0.15$ (K_2SO_4), 25 °C.

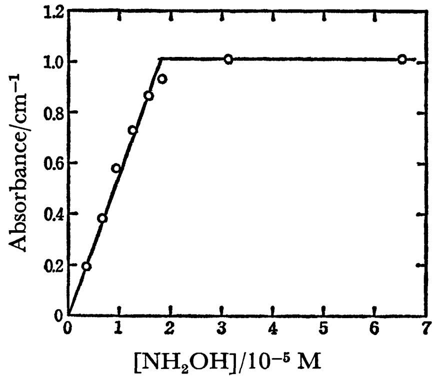

Fig. 2. Stoichiometry of the reaction of Cu(II) with hydroxylamine.
$[Cu(II)]_0=4.03\times10^{-5}$ M, $[BCDS]_0=5.08\times10^{-4}$ M, $\mu=0.15$ (K_2SO_4), pH≃5.7, 25 °C.

Figure 2 indicates that one mole of hydroxylamine reduces two moles of copper(II) to copper(I).[5]

Kinetics. Since no difference in the reaction rate was observed between two combinations of the mixing of the reactants, (A) $\{NH_2OH+BCDS\}+\{Cu(II)\}$ and (B) $\{NH_2OH\}+\{BCDS+Cu(II)\}$, the combination A was mainly used to follow the kinetics. The very fast increase in the absorbance at 483 nm on mixing the solution $\{Cu(II)+NH_2OH\}$ with BCDS indicates a much higher rate of the complex formation of copper(I) with BCDS than that of the redox reaction between copper(II) and hydroxylamine.

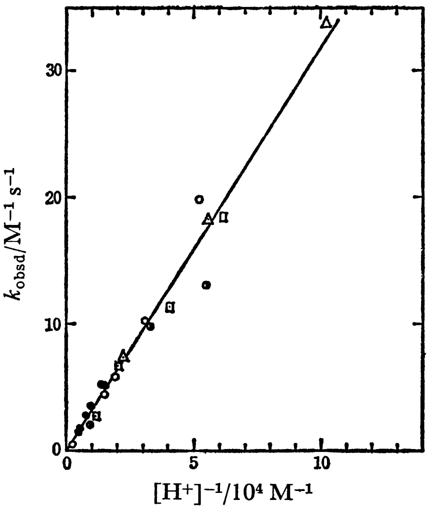

Fig. 3. Plot of the second-order rate constant k_{obsd} against $[\mathrm{H^+}]^{-1}$ at 25 °C.
$[\mathrm{Cu(II)}]_0$, $[\mathrm{BCDS}]_0$, and $[\mathrm{NH_2OH}]_0$ are, ◑: 5.04×10^{-6}, 2.03×10^{-4}, 6.10×10^{-2}; ⊡: 5.04×10^{-6}, 2.03×10^{-4}, 4.58×10^{-2}; ◬: 2.52×10^{-6}, 2.03×10^{-4}, 3.05×10^{-2}; ○: 5.04×10^{-6}, 2.03×10^{-4}, 1.83×10^{-2}; ●: 2.01×10^{-5}, 4.06×10^{-4}, 1.00×10^{-1} M, respectively.

Linear semi-logarithmic plot of the absorbance at 483 nm *vs.* time indicates the first-order dependence on the [Cu(II)] under the conditions $[\mathrm{NH_2OH}]_0 \gg [\mathrm{BCDS}]_0 > [\mathrm{Cu(II)}]_0$. The second-order rate constant k_{obsd} thus obtained depends on the acidity, increasing with $[\mathrm{H^+}]^{-1}$ as shown in Fig. 3.

Following rate law of the redox reaction is thus derived.

$$\frac{1}{2}\cdot\frac{d[\mathrm{Cu^I(BCDS)_2}]}{dt} = -\frac{1}{2}\cdot\frac{d[\mathrm{Cu(II)}]}{dt}$$
$$= k_{\mathrm{obsd}}[\mathrm{NH_2OH}][\mathrm{Cu(II)}]$$
$$= \frac{k_a}{[\mathrm{H^+}]}\cdot[\mathrm{NH_2OH}][\mathrm{Cu(II)}].$$

The apparent rate constant k_a is evaluated to be $3.1\times10^{-4}\,\mathrm{s}^{-1}$ from the slope of the straight line in Fig. 3.

The acid dissociation constants for the aquo copper(II) ion and the hydroxylammonium ion are in the same order of magnitude as $K_H = [\mathrm{CuOH^+}][\mathrm{H^+}]/[\mathrm{Cu^{2+}}] = 10^{-6.47}$ 6) and $k_a = [\mathrm{NH_2OH}][\mathrm{H^+}]/[\mathrm{NH_3OH^+}] = 10^{-5.96}$ 7) at 25 °C.

Although direct evidence for the formation of the complexes of copper(II) with hydroxylamine was not obtained, it would be reasonable to assume the fast formation of copper(II) complex with hydroxylamine followed by the redox reaction, since the observed redox reaction is very slow in comparison with the complex formation of aquo copper(II) ion in general.

The formation of short-lived radical species was reported in the reaction of hydroxylamines with one-electron abstracting oxidants such as cerium(IV).8) Though in the reaction with bivalent copper we have no direct evidence as for the radical formation, we derived the following reaction scheme involving radicals to interpret the above reaction stoichiometries.

$$\begin{tikzcd}
\mathrm{CuSO_4\quad NH_3OH^+} \arrow[d, shift right, "K_1\quad +\mathrm{H^+}\quad K_2(\equiv K_a)"] & \\
\mathrm{Cu^{2+} + NH_2OH} \arrow[u, shift right] \arrow[r, shift left, "K"] \arrow[d, shift right, "K_3(\equiv K_H)"'] & \mathrm{Cu^{II}\cdot NH_2OH} \arrow[l, shift left] \arrow[d, "k_1"] \\
\mathrm{CuOH^+ + H^+} \arrow[u, shift right] & \mathrm{Cu(I) + NH_2O\cdot + H^+}\quad (1)
\end{tikzcd}$$

$$2\mathrm{Cu(II)} + 2\mathrm{NH_2O\cdot} \xrightarrow{k_2} 2\mathrm{Cu(I)} + \mathrm{N_2O} + \mathrm{H_2O} + 2\mathrm{H^+} \quad (2)$$

$$\mathrm{Cu(I)} + 2\mathrm{BCDS} \xrightarrow{\text{fast}} \mathrm{Cu^I(BCDS)_2}. \quad (3)$$

The overall reaction is thus summarized as,

$$4\mathrm{Cu(II)} + 2\mathrm{NH_2OH} + 8\mathrm{BCDS} \longrightarrow 4\mathrm{Cu^I(BCDS)_2} + \mathrm{N_2O} + \mathrm{H_2O} + 4\mathrm{H^+}. \quad (4)$$

In the radical reaction (2), k_2 is postulated to be much larger than k_1K. Thus the k_{obsd} is approximated as follows:

$$k_{\mathrm{obsd}} = \frac{k_a}{[\mathrm{H^+}]} = \frac{k_1K}{[\mathrm{H^+}]\{K_1[\mathrm{SO_4^{2-}}]+1\}+K_3}.$$

Under the experimental conditions, $[\mathrm{H^+}]\{K_1[\mathrm{SO_4^{2-}}]+1\} \gg K_3$, and $[\mathrm{SO_4^{2-}}] = 0.1$ M.

The value of k_1K is evaluated to be $6.2\times10^{-3}\,\mathrm{s}^{-1}$ at 25 °C. The small values of k_a and k_1K may be attributed to the small complex formation constant K.

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5) It was reported2) that dinitrogen oxide was detected by gas chromatography and infrared spectrum as an intermediate of the reaction of cerium(IV) with hydroxylamine in 0.25 M sulfuric acid. We assume the formation of dinitrogen oxide also in the reaction of copper(II) with hydroxylamine.

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