Sterically Controlled Substitution of Copper(II) with 3,3′-Bis[*N,N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein

Mutsuo Yamada

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received December 11, 1975)

The rate constants for the formation of the diprotonated bimetallic complex of copper(II) with 3,3′-bis[*N,N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein (XO) have been determined by the stoppedflow method. The results are interpreted in terms of the reactions, $Cu+LH_2 \rightleftharpoons CuLH_2 \overset{\diagdown Cu}{\rightleftharpoons} Cu_2LH_2$ and $Cu+LH_3 \rightleftharpoons CuLH_2+H \overset{\diagdown Cu}{\rightleftharpoons} Cu_2LH_2+H$. The over-all rate constants, k_1 and k_2 for both reactions are determined to be $k_1=(3.6\pm0.3)\times10^6 M^{-1}s^{-1}$ and $k_2=(8.7\pm1.3)\times10^3 M^{-1}s^{-1}$ at 25.0 °C and $I=0.1$ M.

During a search for establishing the solution chemistry on the metal complexes with XO,[1-3] it has been found that copper(II) ion forms the diprotonated bimetallic complex Cu_2LH_2 with XO in solutions containing an excess of copper(II) ion to XO at pH 3.5—5.5. The structure of the complex has been proposed to be four nine-membered and two eight-membered rings.[2]

In the present paper it is examined by the stopped-flow method how the unfavorable large-membered chelate rings affect the complexation reaction of copper(II) ion with XO.

Experimental

Materials. *Reagents*: All chemicals used are of analytical grade, unless otherwise specified. Water is deionized and distilled.

Xylenol Orange: The acid form of the "*pure*" specimen[4,5] is used. 1×10^{-3} M stock solution of XO is prepared by weight.

Copper(II) Perchlorate: Copper(II) perchlorate is prepared from recrystallized copper(II) chloride by heating with a small excess of perchloric acid. Perchlorate is recrystallized twice from water. The solution is standardized by EDTA titration using PAN as indicator.

Sodium Perchlorate: The purified salt[1] is heated at *ca.* 200 °C to prepare anhydrous salt. The concentration of the solution is determined by weight. The ionic strength of the solution is adjusted to 0.1 M with the sodium perchlorate.

Buffer Solutions: They are prepared from 1.0 M acetic acid and 1.0 M sodium acetate.

Measurements. The rates of complexation reaction are measured at 574 nm, the maximum absorption of Cu_2LH_2 complex,[2] with a Union Giken stopped-flow rapid-scan spectrophotometer Model RA 1300 and their signals are stored in an image dissector and then recorded on a Rigaku Denki transient recorder.

The pH values of the solutions are measured with a Radiometer pH Meter 4d (Copenhagen) equipped with a glass electrode Type G 202B and a saturated calomel electrode Type K 401.

All measurements are made at 25.0±0.2 °C by circulating thermostated water from a Lauda Type K 2R Electronic with a circular Duplex pumps.

Results

Figure 1 shows the plot of k_{obsd}, the apparent first-order rate constant, against the total concentration of copper(II) ion for the total concentration of XO, $T_L=1.60\times10^{-5}$ M at pH 3.87—5.36 at 25.0 °C and $I=0.1$ M. As k_{obsd} is the first-order with respect to copper(II) ion at each value of pH, the following equation holds

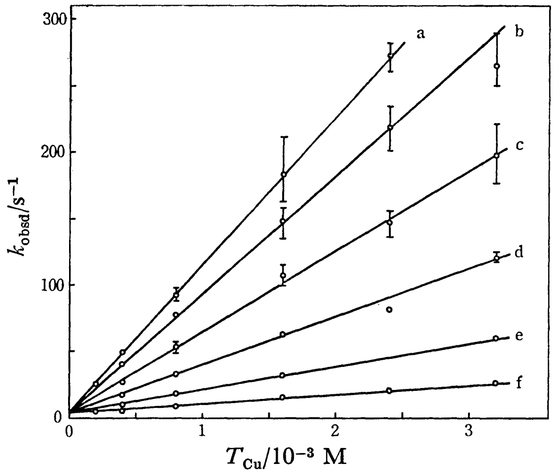

Fig. 1. Plot of k_{obsd} against the total concentration of copper(II) ion at various pH values in the formation of Cu_2LH_2 for $T_L=1.60\times10^{-5}$ M, at 25.0 °C and $I=0.1$ M. pH: a) 5.36±0.04, b) 5.17±0.03, c) 4.97±0.03, d) 4.70±0.04, e) 4.27±0.07, and f) 3.87±0.09.

$$k_{obsd} = k_f[Cu] + k_d, \qquad (1)$$

where k_f and k_d are the forward and the reverse rate constants of the reaction, respectively.

In the above pH region, the protolytic equilibria of the ligand are

$$LH_2 + H \rightleftharpoons LH_3;\ K_1 = 10^{6.74} \qquad (2)$$

$$LH_3 + H \rightleftharpoons LH_4;\ K_2 = 10^{2.85}, \qquad (3)$$

where K_1 and K_2 are the acid-association constants[6] of the ligand at 25.0 °C and $I=0.1$ M.

The kinetic data are consistent with the assumption that the formation of Cu_2LH_2 proceeds *via* two paths in Eqs. 4 and 5 and that the protolytic reactions of Eqs. 2 and 3 reach equilibria much faster than the metal complex reactions

$$Cu + LH_2 \rightleftharpoons CuLH_2 \overset{\diagdown Cu}{\rightleftharpoons} Cu_2LH_2;\ k_1 \qquad (4)$$

$$Cu + LH_3 \rightleftharpoons CuLH_2 + H \overset{\diagdown Cu}{\rightleftharpoons} Cu_2LH_2 + H;\ k_2, \qquad (5)$$

where $CuLH_2$ is a terdentate intermediate **4** in Fig. 3.

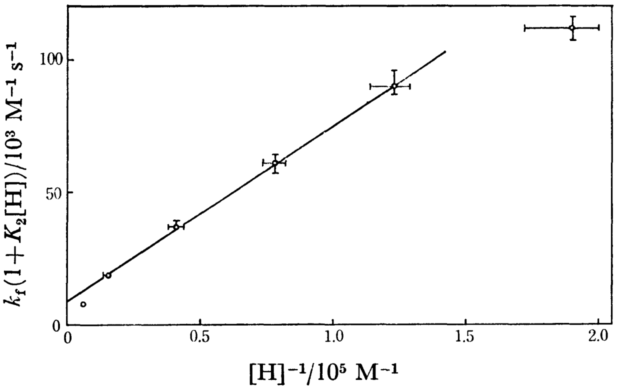

Fig. 2. Plot of $k_f(1+K_2[H])$ against the inverse of hydrogen ion concentration in the formation of Cu_2LH_2 at 25.0 °C and $I=0.1$ M.

The forward rate of the formation of Cu_2LH_2 is given by

$$d[Cu_2LH_2]/dt = k_f[Cu]C_L$$
$$= k_1[Cu][LH_2] + k_2[Cu][LH_3], \tag{6}$$

where

$$C_L = [LH_4] + [LH_3] + [LH_2], \tag{7}$$

and k_1 and k_2 are the over-all forward rate constants of the reactions for (4) and (5), respectively.

From Eqs. 6 and 7, the formation rate constant k_f is expressed by the equation

$$k_f = (k_1+k_2K_1[H])/(1+K_1[H]+K_1K_2[H]^2). \tag{8}$$

Plot of $k_f(1+K_2[H])\times10^3$ against $[H]^{-1}\times10^5$ gives a straight line (Fig. 2). From Eq. 8 the relation $k_f(1+K_2[H])=k_2+k_1/K_1[H]$ holds in the experimental pH region. The intercept and the slope give the values of k_2 and k_1/K_1, respectively. The values of k_1 and k_2 are evaluated to be $k_1=(3.6\pm0.3)\times10^6$ M^{-1}s^{-1} and $k_2=(8.7\pm1.3)\times10^3$ M^{-1}s^{-1} at 25.0 °C and $I=0.1$ M.

Discussion

From equilibrium measurements it has been found that copper(II) ion forms the diprotonated *bimetallic* complex with XO,[2] while from kinetic measurements of the complexation reaction of copper(II) ion with XO, k_{obsd} is found to be the first-order with respect to copper(II) ion. These facts indicate that on complexation of copper(II) ion with XO two copper(II) ions do not simultaneously react with two different coordinating sites of XO but successively react with them to form the diprotonated *bimetallic* complex. Thus following mechanisms are considered (Fig. 3).

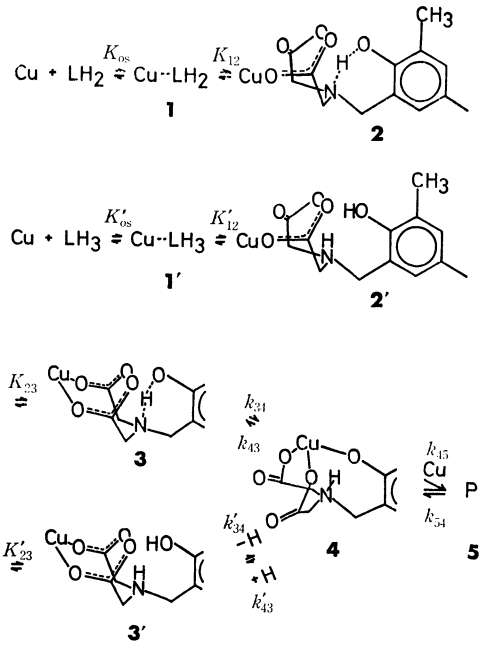

Fig. 3. Proposed mechanisms of the formation of Cu_2-LH_2.

Using steady-state approximation for species **3** and **4** (**3′** and **4**), and assuming rapid equilibria between species **1** and **2** (**1′** and **2′**), and assuming $k_{45}[Cu]\gg k_{43}$ ($k'_{45}[Cu]\gg k'_{43}$) and $k_{32}\gg k_{34}$ ($k'_{32}\gg k'_{34}$) one gives the expression for the forward rate constant at each value of pH in Eq. 9

$$k_f = k_{34}K_{os}K_{12}K_{23}[Cu][LH_2]$$
$$+ k'_{34}K'_{os}K'_{12}K'_{23}[Cu][LH_3]. \tag{9}$$

From Eqs. 6 and 9,

$$k_1 = k_{34}K_{os}K_{12}K_{23} \tag{10}$$

$$k_2 = k'_{34}K'_{os}K'_{12}K'_{23}. \tag{11}$$

As the value of the product $K_{os}K_{12}$ is approximately estimated to be 78 M^{-1} from the stability constant of the copper(II) acetate,[7] the value of the product $k_{34}K_{23}$ is calculated to be 4.6×10^4 s^{-1}. If K_{23} is estimated from the ratio of the copper(II) complexes with malonic acid[7] and acetic acid,[7] K_{23} is calculated to be 4.6×10^3. Thus k_{34} is approximately evaluated to be 10 s^{-1}.

It is due to the small value of k_{34} that the value of k_1 (3.6×10^6 M^{-1}s^{-1}) is smaller by approximately 3 orders of magnitude than those of the rate constants of the normal substitution reaction of aquo copper(II) ion with the ligands.

It is found that the formation of large-membered chelate rings reduces the rate of the substitution reaction. Kustin *et al.* have termed the reactions like this "*sterically controlled substitution*," the rate has been shown to be ligand dependent.[8]

The author should like to thank Professor M. Fujimoto for general discussion and reading the manuscript.

References

1) M. Yamada and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, to be published. "The Solution Chemistry for Complexes of Nickel(II) and Cobalt(II) with 3,3′-Bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein."

2) M. Yamada, *Bull. Chem. Soc. Jpn.*, to be published. "Diprotonated Bimetallic Complex between Copper(II) with 3,3′-Bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein."

3) M. Yamada and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, to be published.

4) M. Yamada and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **44**, 294 (1971).

5) M. Yamada and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, to be published. "Preparative Thin-Layer Chromatography

of Semi-Xylenol Orange and Xylenol Orange by Developing with Solvents Giving Discrete pH Change on the Plate."

6) M. Murakami, T. Yoshino, and S. Harasawa, *Talanta*, **14**, 1293 (1967).

7) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes, Supplement No. 1," Special Publication, No. 25, The Chemical Society, London (1970).

8) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.*, **88**, 4610 (1966); A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *ibid.*, **89**, 3126 (1967); R. F. Pasternack and K. Kustin, *ibid.*, **90**, 2295 (1968).