BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2723—2724 (1979)

Thermochromism of Metal Chelates with Triphenylmethane Complexons in Aqueous Solutions. II. Inhibitive Effects of the Protolysis of Aqua Cu^{2+} Ion on the Thermochromism of Cu(II)–Xylenol Orange Chelate

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(Received January 18, 1979)

Synopsis. Temperature-dependent protolytic equilibrium, $Cu(OH_2)_n^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu(OH)(OH_2)_{n-1}^{+} + H^+$, was found to inhibit thermochromic changes of Cu(II)–Xylenol Orange (XO) chelate in unbuffered weakly acid aqueous solutions. The rate constants, k_1 and k_{-1}, at 25 °C and I=0.1 mol dm^{-3} were evaluated to be 10^3—10^4 s^{-1} and *ca.* 2×10^9 mol^{-1} dm^3 s^{-1}, respectively.

In previous papers we reported the thermochromism of the metal chelates of triphenylmethane complexons in aqueous solutions.[1] For the Cu(II)–XO complex the observed thermochromism was primarily ascribed to the temperature-dependent acid-dissociation equilibria between two 2 : 1 Cu(II)–XO chelates, AH and A: $AH \rightleftharpoons A+H$, where AH denotes a complex species having an uncoordinated free phenolic hydroxyl group and A a complex species having a coordinated phenolate group,[1] the charges being omitted. In unbuffered weakly acid aqueous solutions containing a large excess of Cu(II) ion the thermochromic change was not observed. In the present communication we aim to solve the problems on this phenomenon based on the spectrophotometric and the temperature-jump measurements.

Figure 1 shows the absorption spectra at various temperatures of an unbuffered aqueous solution containing 500-fold excess of Cu(II) ion over XO (2×10^{-5} mol dm^{-3}). With the rise of temperature from 15 to 60 °C the absorbance at 574 nm increases only by 7% and the thermochromic change was not observed.** The pH of the solution varies from 4.86 at 15 °C to 4.46 at 60 °C. On the basis of the values of ΔH and ΔS determined for the equilibrium $AH \rightleftharpoons A+H$,[1] only a negligibly small change in pH should be expected. The large decrease in pH observed above strongly suggests the possibility of a contribution of the temperature-dependent protolysis of a large excess of Cu^{2+} ion. This possibility was proved based on the temperature-jump data for aqueous solutions of Cu(II) ion containing uncomplexing acid-base indicators, Bromocresol Green (BCG), Bromocresol Purple (BCP), and Bromophenol Blue (BPB).

The pH of unbuffered solution containing 2×10^{-5} mol dm^{-3} BCG and 1×10^{-2} mol dm^{-3} $Cu(ClO_4)_2$ varied from 5.40 at 14 °C to 5.10 at 60 °C, and the absorbance at 628 nm, the λ_{max} of BCG, markedly decreased with the rise of temperature.

Figures 2(a) and 2(b) show the typical relaxation signals observed for the unbuffered systems, Cu(II)–XO and Cu(II)–BCG, respectively. In the Cu(II)–XO system, a fast relaxation signal of an increasing absorbance at 574 nm was observed in 5 µs region,

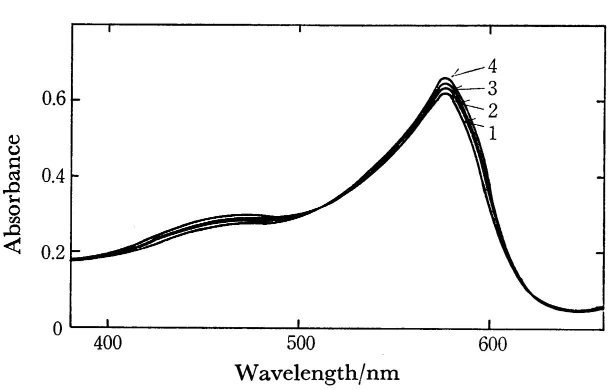

Fig. 1. Absorption spectra of an aqueous solution of Cu(II)-XO. At 15 (1), 25 (2), 44 (3), and 60 °C (4). $[Cu]_0=1.0\times10^{-2}$ and $[XO]_0=2\times10^{-5}$ mol dm^{-3} ([ ]$_0$ denotes the total concentration). I= 0.1 mol dm^{-3} (NaClO$_4$). The pH of the solution varied from 4.86 (15 °C) to 4.46 (60 °C).

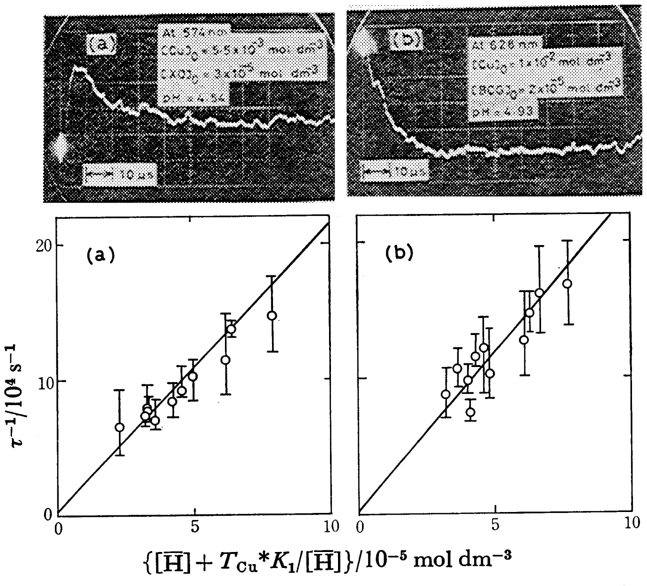

Fig. 2. Temperature-jump signals and the plots of τ^{-1} *vs.* $([\overline{H}]+T_{Cu}{}^*K_1/[\overline{H}])$ at 25 °C and I=0.1 mol dm^{-3} (NaClO$_4$) for Cu(II)-XO (a) and Cu(II)-BCG (b).

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** In the case of a solution of the same pH containing only a small excess of Cu(II) ion over XO the absorbance at 574 nm increased so markedly as *ca.* 30% even in unbuffered systems.[1]

TABLE 1. THE RATE CONSTANTS, k_1 AND k_{-1}, FOR THE PROTOLYTIC REACTION, $\mathrm{Cu(OH_2)}_n^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu(OH)(OH_2)}_{n-1}^{+} + \mathrm{H}^+$ (I=0.1 mol dm^{-3} ($\mathrm{NaClO_4}$))

X	$k_1/10^4\ \mathrm{s^{-1}}$	$k_{-1}/10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$	T/K
XO	1.4±1.0	1.8±0.3	298
BCG	1.0±0.9	1.3±0.5	290
	2.4±2.0	2.0±0.4	298

prior to a slower signal in 10 μs region indicating a decrease in the absorbance (Fig. 2(a)). The signal in the 5 μs region corresponds to the fast protonation-deprotonation $\mathrm{AH} \rightleftharpoons \mathrm{A} + \mathrm{H}$.[1] The slower relaxation signal is ascribed to the protolysis of Cu^{2+} ion coupled with the fast thermochromic change of the Cu(II)–XO system. In the Cu(II)–GCB system, however, the fast relaxation signal in the region of 5 μs was not observed, only the slower signal was invariably observed in the 10 μs region (Fig. 2(b)). The slower signals observed in both systems are interpreted as a process involving the protolysis of the excess of Cu^{2+} ion.[2]

Assuming pre-equilibria for the thermochromic changes of the Cu(II)–XO system and also for the protonation-deprotonation process of the indicator, and regarding the protolysis of the Cu^{2+} ion in the unbuffered aqueous solution as a rate-determining step, we describe the given coupled reactions by the following two-step mechanism:

$$\mathrm{HX} \overset{K_x}{\rightleftharpoons} \mathrm{H} + \mathrm{X} \tag{1}$$

and

$$\mathrm{Cu(OH_2)}_n^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu(OH)(OH_2)}_{n-1}^{+} + \mathrm{H}^+, \tag{2}$$

where X denotes the base form of the chelate, A, or that of the acid-base indicator, In, and $K_x = K_a$ or K_{In}. In Eq. 1 the charges are omitted. With appropriate assumptions on the experimental conditions the relaxation time τ observed in the 10 μs region can be expressed as Eq. 4:

$$\tau^{-1} = k_1 + k_{-1}\left\{[\overline{\mathrm{H}}] + [\overline{\mathrm{CuOH}}] \cdot \frac{[\overline{\mathrm{H}}] + K_x}{[\overline{\mathrm{X}}] + [\overline{\mathrm{H}}] + K_x}\right\} \tag{3}$$

$$\simeq k_1 + k_{-1}\left\{[\overline{\mathrm{H}}] + \frac{T_{\mathrm{Cu}}{}^*K_1}{[\overline{\mathrm{H}}]}\right\}, \tag{4}$$

where T_{Cu} denotes the total concentration of Cu(II), and $^*K_1 = [\overline{\mathrm{CuOH}}][\overline{\mathrm{H}}]/[\overline{\mathrm{Cu}}] = 10^{-7.34}$.[3] $[\overline{\ }]$ denotes the equilibrium concentration. CuOH indicates the deprotonated species, $\mathrm{Cu(OH)(OH_2)}_{n-1}^{+}$.

The plots of τ^{-1} against $[\overline{\mathrm{H}}] + T_{\mathrm{Cu}}{}^*K_1/[\overline{\mathrm{H}}]$ give fairly good straight lines for both systems, Cu(II)–XO and Cu(II)–BCG (Figs. 2(a) snd 2(b)). Table 1 shows the values of the rate constants, k_1 and k_{-1}, for the protolytic reaction (2) estimated from the intercepts and the slopes of the straight lines. The estimated value of k_{-1} ($\simeq 2\times10^9\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$) lies nearly in the order of magnitude of the rate constant for the recombination of $\mathrm{CuOH^+}$ and $\mathrm{H^+}$ reported by Eigen *et al.* based on the sound absorption measurements ($k_{-1} \simeq 1\times10^{10}\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$).[4] The value of $^*K_1$ derived from the ratio k_1/k_{-1}, however, varies in the range 10^{-5} —10^{-7} mol dm^{-3} owing to the large errors inherent in the estimation of the intercepts.

The system Cu(II)–BCP gave a slower relaxation signal in the 10 μs region only in the pH-region 5.2—5.9. In this system no linear relationship was obtained, presumably due to the contribution of the dimer formation in the Cu(II) species above pH 5.5.

As regards the Cu(II)–BCG system we estimated the activation enthalpies for k_1 and k_{-1} to be $\Delta H^{*}_{+} = 19$ kcal mol^{-1} and $\Delta H^{*}_{-} = 9$ kcal mol^{-1}, respectively. The difference in the values, 10 kcal mol^{-1}, agrees well with the value of ΔH for the protolytic equilibrium (2), 10—12 kcal mol^{-1}.[3]

On the basis of the results mentioned above we ascribe the observed inhibition of the thermochromism of Cu(II)–XO chelate in the presence of a large excess of Cu(II) ion in unbuffered aqueous solutions to the protolysis of the excess of aqua Cu^{2+} ion.

Experimental

A highly purified specimen of 3,3′-bis[*N*,*N*-bis(carboxymethyl) aminomethyl]-*o*-cresolsulfonaphthalein (Xylenol Orange) was used throughout the present work.[5] Reagent grade acid-base indicators, BCG, BCP, and BPB (Wako), were used. The pH values of the unbuffered solutions were adjusted with $\mathrm{HClO_4}$ and NaOH (0.1 mol dm^{-3}) in the ranges 4.0—5.2, 4.4—5.2, and 4.3—5.9 for Cu(II)–BCG, –BPB, and –BCP systems, respectively. In the case of buffered systems, acetate, citrate, and phthalate buffers were used. The details on the measurements using a co-axialcable temperature-jump apparatus were described in a previous paper.[6]

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