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The Effect of 1,10-Phenanthroline on the Rate of Xylenol Orange Indicator Color Change

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1,10-Phenanthroline(phen) accelerates the rate of the color change of Xylenol Orange(XO) in the copper(II)–EDTA titrations due to the formation of a mixed-ligand complex, (Cuphen)$_2$xo. The rate of the substitution reaction of Cu$_2$xo with 1,10-phenanthroline or with EDTA in the presence of 1,10-phenanthroline has been determined by the stopped-flow method over the pH range of 6.9—7.6 at $\mu=0.1$ (KNO$_3$) and 25±1 °C. At 6.2×10^{-5}—1.2×10^{-3}M 1,10-phenanthroline, the rate-law is expressed as $-\mathrm{d}[(\mathrm{Cu_2xo})']/\mathrm{d}t=k_1[\mathrm{H}][(\mathrm{Cu_2xo})']$. The reaction mechanism proposed is $\mathrm{Cu_2xo}\xrightarrow{\text{2phen}}(\mathrm{Cuphen})_2\mathrm{xo}\overset{\mathrm{H^+}}{\rightleftharpoons}(\mathrm{Cuphen})_2\mathrm{xo}\cdots\mathrm{H}\xrightarrow{\text{r.d.s.}}\mathrm{Cuphen}+(\mathrm{Cuphen})\mathrm{Hxo}\xrightarrow{\text{fast}}$ 2Cuphen+xo′, and $k_1=5.5\times10^7\ \mathrm{M^{-1}\ s^{-1}}$. By the addition of 2.5×10^{-6}—10^{-5} M 1,10-phenanthroline, copper(II) can be titrated with EDTA at room temperature with XO as an indicator.

In the copper(II)–EDTA titrations with Xylenol Orange (XO) as an indicator, hexamine slows down the rate of the color change of XO. The mechanism of the color change was reported in our previous paper.[1] On the other hand, 1,10-phenanthroline accelerates the rate of color change of the XO indicator remarkably.[2,3] This may be due to the mixed-ligand complex formation of the Cu$_2$xo chelate with 1,10-phenanthroline, and it may contribute to the color change as in the case of PAN.[4]

In this paper the composition of the mixed-ligand complexes of Cu–XO–phen and the rate of the substitution reaction of Cu–XO–phen with EDTA are determined, and the acceleration mechanism of the color change of XO by 1,10-phenanthroline is discussed.

Experimental

Reagents. XO was synthesized by the published method.[5,6] The solvent of the reaction product was distilled off under reduced pressure, and crude XO was obtained. The fractional precipitation of XO from the reaction mixture with ethanol[5,6] gives a lower yield of XO because of decomposition. The pure XO was completely separated on a cellulose column(prepared with Toyo-Roshi cellulose powder) by elution with butyl alcohol saturated with 10% acetic acid. The free-acid form(H$_6$xo) was obtained by passing the solution of the sodium salt through a column of Dowex 50W-X8(H$^+$) cation-exchange resin(100—200 mesh). The purity of H$_6$xo was estimated to be almost 100% by means of paper chromatography, pH-titration with a standard sodium hydroxide solution, and spectrophotometric titration with a standard copper(II) solution.

The 1,10-phenanthroline was recrystallized from an ethanol-water solution.

The other reagents employed were the same as those reported previously.[1]

The following buffers were used for adjusting the pH: pH 6.8—7.6: 0.02 M 3-morpholino-1-propanesulfonic acid(MOPS)–NaOH; pH$<$6.8: 0.02 M 2-morpholino-1-ethanesulfonic acid(MES)–NaOH. MOPS and MES were obtained from Dojindo Laboratories, Kumamoto, Japan.

The ionic strength was kept at 0.1 with KNO$_3$.

All the experiments were carried out at 25±1 °C.

Apparatus. A Union Giken Stopped-Flow Spectrophotometer, Type RA-401, a Union Giken High Sensitivity Spectrophotometer, Type SM-401, a Hitachi Spectrophotometer, Type 124, and a Radiometer pH Meter, Type PHM 26c, were used.

Results

Mixed-Ligand Complexes of Cu$_2$xo with 1,10-Phenanthroline. In the presence of more than a 2-fold excess of copper(II), XO forms the Cu$_2$xo chelate above pH 5.5; the absorption maximum appears at 574 nm. When 1,10-phenanthroline (phen) was added to the Cu$_2$xo solution, the absorption maximum shifted to a longer wavelength (585 nm) and the molar absorp-

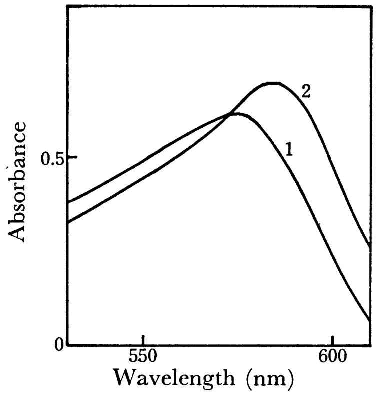

Fig. 1. Absorption spectra of Cu$_2$xo and (Cuphen)$_2$xo. $C_{\mathrm{XO}}=1.32\times10^{-5}$ M, $C_{\mathrm{Cu}}=2.58\times10^{-5}$ M, (1) Cu$_2$xo, pH 6.04; (2) (Cuphen)$_2$xo, $C_{\mathrm{phen}}=3.29\times10^{-5}$ M, pH 7.00.

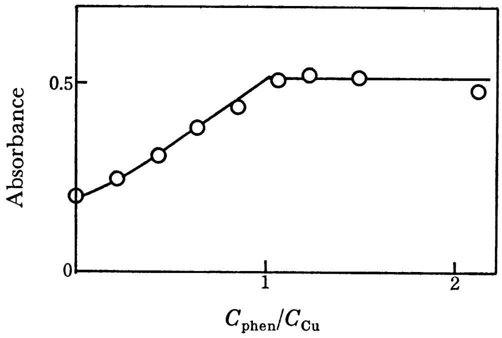

Fig. 2. Molar-ratio method of the mixed-ligand complex. $C_{\mathrm{XO}}=1.32\times10^{-5}$ M, $C_{\mathrm{Cu}}=2.58\times10^{-5}$ M, pH 6.93.

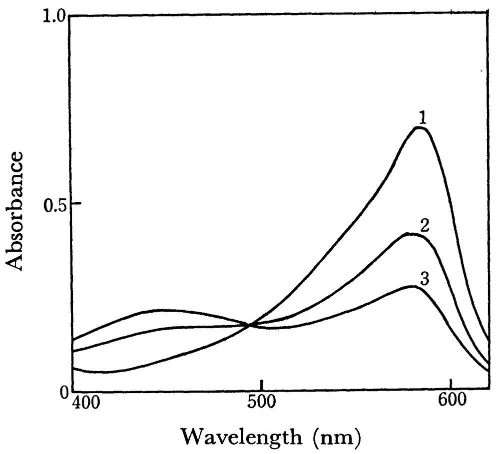

Fig. 3. Absorption spectra of the mixed-ligand complexes at different pH.
$C_{XO}=1.32\times10^{-5}$ M, $C_{Cu}=2.58\times10^{-5}$ M, $C_{phen}=3.29\times10^{-5}$ M, pH: (1) 7.00; (2) 5.98; (3) 5.50.

tivity increased by about 20% compared to that of Cu_2xo (Fig. 1). By the molar-ratio method it was found that $(Cuphen)_2xo$ was formed (Fig. 2).

The absorption spectra of a copper–XO chelate solution containing a 2.5-fold amount of 1,10-phenanthroline at different pH values are shown in Fig. 3. The absorption maximum shifts from 440 to 585 nm with an increase in the pH, an isosbestic point appears at 492 nm. Since copper(II) forms the Cu_2Hxo chelate with an absorption maximum at 444 nm at pH values lower than 4.5 in the absence of 1,10-phenanthroline, it is clear that $(Cuphen)_2Hxo$ is formed at lower pH values and that a proton may dissociate with an increase in pH. Thus, the following equilibrium exists in the pH range between 4.5 and 7.0:

$$(Cuphen)_2Hxo^- \rightleftarrows (Cuphen)_2xo^{2-} + H^+. \tag{1}$$

The equilibrium constant,

$$K^{H}_{(Cuphen)_2Hxo} = \frac{[(Cuphen)_2Hxo]}{[(Cuphen)_2xo][H]},$$

was evaluated to be $10^{5.7}$ from the change in the absorbance at 585 nm with the pH. The dissociation of the proton in $(Cuphen)_2Hxo$ is more difficult than that in Cu_2Hxo ($K^{H}_{Cu_2Hxo}=10^{4.55}$).[1)]

The Substitution Reaction of Cu_2xo with 1,10-Phenanthroline. The rate of the substitution reaction of Cu_2xo with a large excess of 1,10-phenanthroline was measured by the stopped-flow method. Figure 4 shows a plot of the absorbance at 580 nm against the reaction time. The rapid increase in the absorbance at beginning indicates the formation of the mixed-ligand complex $(Cuphen)_2xo$. Then the reaction proceeds as

$$Cu_2xo^{2-} + 2phen \longrightarrow (Cuphen)_2xo^{2-}, \tag{2}$$

$$(Cuphen)_2xo^{2-} + 4phen \longrightarrow 2Cu(phen)_3{}^{2+} + xo'. \tag{3}$$

Under the present experimental conditions, the substitution reaction proceeds to completion and the reverse reaction can be neglected. The rate law may be expressed as:

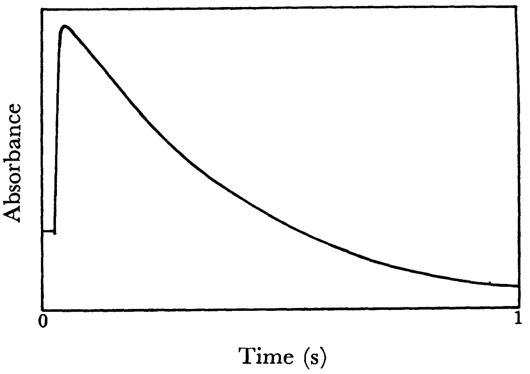

Fig. 4. Substitution reaction of Cu_2xo with 1,10-phenanthroline.
$C_{XO}=1.22\times10^{-5}$ M, $C_{Cu}=2.27\times10^{-5}$ M, $C_{phen}=8.67\times10^{-4}$ M, pH 7.43, 580 nm.

$$-\frac{d[(Cu_2xo)']}{dt} = k_{0(H,phen)}[(Cu_2xo)'], \tag{4}$$

where $[(Cu_2xo)']$ is the total concentration of copper–XO complexes and $k_{0(H,phen)}$ is the conditional rate constant involving the concentrations of the hydrogen ion and 1,10-phenanthroline. Representing the absorbances at the reaction times of 0, t, and ∞ as A_0, A_t, and A_∞ respectively, we obtain from Eq. 4

$$\log(A_t-A_\infty) = -\frac{k_{0(H,phen)}}{2.303}t + \log(A_0-A_\infty). \tag{5}$$

The experiments were carried out under the conditions where $C_{XO}=1.22\times10^{-5}$ M, $C_{Cu}=2.27\times10^{-5}$ M, and $C_{phen}=(6.19—12.4)\times10^{-4}$ M, pH 6.89—7.60. The rate plots of $\log(A_t-A_\infty)$ *vs.* t were linear for at least 90% of the reactions. The data in Table 1 indicate that the values of $k_{0(H,phen)}$ are proportional to the hydrogen-ion concentration, but independent of the 1,10-phenanthroline concentration; *i.e.*,

TABLE 1. FIRST-ORDER CONDITIONAL RATE CONSTANTS $k_{0(H,phen)}$
$C_{XO}=1.22\times10^{-5}$ M, $C_{Cu}=2.27\times10^{-5}$ M, 25 °C, $\mu=0.1$.

pH	$C_{phen}(\times10^{-4}$ M)	$k_{0(H,phen)}$ (s^{-1})
6.89	6.19	7.48
	7.43	7.48
	8.67	7.48
	9.90	7.36
	11.1	7.48
	12.4	7.48
6.94	6.19	6.10
	7.43	6.18
	8.67	6.13
	9.90	6.13
7.04	6.19	5.06
	8.67	5.18
7.19	7.43	3.33
	8.67	3.33
7.43	6.19	2.42
	8.67	2.50
7.60	6.19	1.80
	7.43	1.80
	8.67	1.78

$$k_{0(\mathrm{H,phen})} = k_1[\mathrm{H}]. \qquad (6)$$

This result indicates that the equilibrium (Eq. 2) shifts to the right completely and that the following reaction is the rate-determining step:

$$(\mathrm{Cuphen})_2\mathrm{xo}^{2-} + \mathrm{H}^+ \rightleftharpoons \mathrm{H}\cdots\mathrm{xo}(\mathrm{Cuphen})_2 \xrightarrow{\text{r.d.s.}} (\mathrm{Cuphen})\mathrm{Hxo}^{3-} + \mathrm{Cuphen}^{2+}. \qquad (7)$$

The resulting (Cuphen)Hxo may undergo rapid substitution with 1,10-phenanthroline. The rate constant, k_1, was evaluated as 5.5×10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

The Substitution Reaction of Cu_2xo with EDTA in the Presence of 1,10-Phenanthroline. When a large excess of 1,10-phenanthroline is added to a Cu_2xo solution the substitution proceeds and the absorbance of Cu–XO complex decreases. The substitution of Cu_2xo with a solution containing a large excess of EDTA and (6.0—24.8) $\times 10^{-5}$ M phenanthroline was, then, carried out. The rate expression is given as

$$-\frac{\mathrm{d}[(\mathrm{Cu_2xo})']}{\mathrm{d}t} = k_{0(\mathrm{EDTA,H,phen})}[(\mathrm{Cu_2xo})']. \qquad (8)$$

TABLE 2. FIRST-ORDER CONDITIONAL RATE CONSTANTS $k_{0(\mathrm{EDTA,H,phen})}$

$C_{XO}=1.22\times10^{-5}$ M, $C_{Cu}=2.27\times10^{-5}$ M, 25 °C, $\mu=0.1$.

C_{EDTA} ($\times 10^{-4}$ M)	C_{phen} ($\times 10^{-5}$ M)	pH	$k_{0(\mathrm{EDTA,H,phen})}$ (s^{-1})
4.48	6.20	6.92	6.49
	12.4		6.90
	18.4		6.96
	24.8		6.77
	3.71	7.00	5.46
	4.21		5.46
	6.20	7.28	3.07
	12.4		2.88
	18.4		3.02
	24.8		2.90
	6.20	7.48	1.87
	12.4		1.84
6.73			2.01
8.97			2.01
11.2			1.96

In this case, the values of $k_{0(\mathrm{EDTA,H,phen})}$ in Table 2 were proportional to only the concentration of the hydrogen ion, just as in the case of the substitution with 1,10-phenanthroline. Therefore, the mechanism of the substitution reaction of Cu_2xo is the same as that in the case of phenanthroline, and (Cuphen)Hxo may undergo rapid substitution with EDTA. The rate constant was obtained as 5.5×10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is in good agreement with the value obtained in the preceding section.

TABLE 3. FIRST-ORDER CONDITIONAL RATE CONSTANTS $k_{0(\mathrm{EDTA,H,phen})}$

$C_{XO}=1.32\times10^{-5}$ M, $C_{Cu}=2.58\times10^{-5}$ M, 25 °C, $\mu=0.1$.

C_{EDTA} ($\times 10^{-4}$ M)	C_{phen} ($\times 10^{-5}$ M)	pH	$k_{0(\mathrm{EDTA,H,phen})}$ (s^{-1})
5.61	2.74	6.89	4.02
		7.05	2.96
		7.25	1.92
	3.29	6.89	4.68
		7.05	3.26
		7.25	2.11
	3.84	6.89	4.76
		7.05	3.35
		7.25	2.30
6.73	3.29	7.05	3.22
7.85			3.22
8.97			3.22

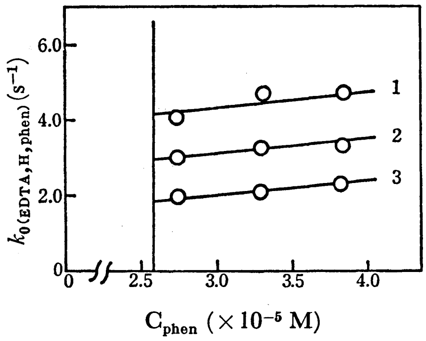

Fig. 5. Plots of $k_{0(\mathrm{EDTA,\,H,\,phen})}$ *vs.* C_{phen}. $C_{XO}=1.32\times10^{-5}$ M, $C_{Cu}=2.58\times10^{-5}$ M, $C_{EDTA}=5.61\times10^{-4}$M, pH: (1) 6.89; (2) 7.05; (3) 7.25.

The substitution under conditions which are very close to those in practical titrations was examined; *i.e.*, a solution containing Cu_2xo and a 2.1—3-fold excess of phenanthroline was replaced with a large excess of EDTA. The values of $k_{0(\mathrm{EDTA,H,phen})}$ are shown in Table 3. We observed no dependence of $k_{0(\mathrm{EDTA,H,phen})}$ on the concentration of EDTA, but a linear relation to the hydrogen ion with the zero intercept and the 1,10-phenanthroline with an intercept were observed (Fig. 5). From these results the following equation is deduced:

$$k_{0(\mathrm{EDTA,H,phen})} = (k_1+k_2[\mathrm{phen}])[\mathrm{H}]. \qquad (9)$$

Under those experimental conditions the mixed-ligand complex $(\mathrm{Cuphen})_2\mathrm{xo}$ may not be formed completely and a small amount of $(\mathrm{Cu_2phen})\mathrm{xo}$ exists, so the second term in Eq. 9 is due to the following equilibrium preceding the rate-determining step (Eq. 7):

$$(\mathrm{Cu_2phen})\mathrm{xo}^{2-} + \mathrm{phen} \rightleftharpoons (\mathrm{Cuphen})_2\mathrm{xo}^{2-}. \qquad (10)$$

Consequently, the substitution mechanism is virtually the same as that with 1,10-phenanthroline.

Discussion

As has been reported previously,[1] for the substitution reaction of Cu_2xo with EDTA the rate-law is expressed by

$$-\frac{\mathrm{d}[\mathrm{Cu_2xo}]}{\mathrm{d}t} = k[\mathrm{Cu_2xo}][\mathrm{edta}'], \qquad (11)$$

and the reaction mechanism is as follows:

$$\mathrm{Cu_2xo}^{2-} + \mathrm{edta}' \rightleftharpoons \mathrm{edta}\cdots\mathrm{Cu(xo)Cu} \xrightarrow{\text{r.d.s.}} \mathrm{Cu(edta)}^{2-} + \mathrm{CuHxo}^{3-}, \qquad (12)$$

$$\mathrm{CuHxo}^{3-} + \mathrm{edta}' \xrightarrow{\text{fast}} \mathrm{Cu(edta)}^{2-} + \mathrm{xo}'. \qquad (13)$$

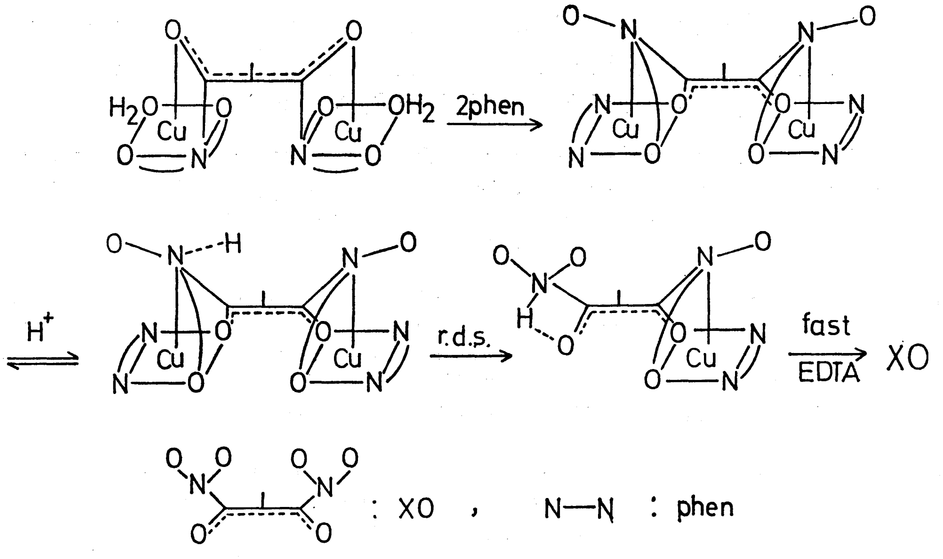

Fig. 6. Proposed reaction mechanism for substitution of (Cuphen)$_2$xo with EDTA.

EDTA coordinates with one of the two coppers in the Cu$_2$xo chelate, and the release of the first copper ion from the intermediate edta···Cu(xo)Cu may be the rate-determining step, while the resulting CuHxo undergoes a rapid substitution with EDTA.

When 1,10-phenanthroline is present, the copper–XO chelate forms a mixed-ligand complex with 1,10-phenanthroline, and it may have a distorted octahedron structure, just as in the case of the copper–PAN–phen mixed-ligand complex.[4] Therefore, the release of the first copper from the (Cuphen)$_2$xo chelate by the attack of a hydrogen ion on one of the nitrogen atoms in the iminodiacetic acid groups may be the rate-determining step (Fig. 6).

In practical titrations of copper(II) with EDTA, the rate of the color change of the XO indicator depends on the concentration of 1,10-phenanthroline and the titration pH. The rates of color change in the presence and in the absence of 1,10-phenanthroline were compared at pH 6.1 (MES buffer) using the stopped-flow spectrophotometer. A solution of copper (1.03×10^{-3} M) containing XO (1.22×10^{-5} M) and 1,10-phenanthroline and a solution containing EDTA (1.04×10^{-3} M, *i.e.* a 1% excess) were rapidly mixed. Usually in a visual titration 90% of the indicator transition is recognized as a complete color change; therefore, the time required for a 90% color transition was measured (Table 4). In the presence of 2.7×10^{-6} M 1,10-phenanthroline the rate of color change is 20-times as much as that in the absence, and with 1.2×10^{-5} M the rate increases by 50-times. Thus, 2.5×10^{-6}—10^{-5} M of 1,10-phenanthroline is sufficient for titration at room temperature. The addition of a larger amount of 1,10-phenanthroline may cause an underconsumption of EDTA.

TABLE 4. EFFECT OF 1,10-PHENANTHROLINE ON THE RATE OF COLOR CHANGE

	Concentration of 1,10-phenanthroline (M)				
	0	2.7×10^{-6}	6.2×10^{-6}	1.2×10^{-5}	2.4×10^{-5}
Time for 90% color change (s)	63	3.3	1.6	1.2	0.7

XO=1.22×10^{-5} M, Cu=1.03×10^{-3} M, EDTA=1.04×10^{-3} M, pH 6.1 (MES buffer), λ=580 nm, μ=0.1, 25 °C.

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References

1) H. Wada, T. Ishizuki, and G. Nakagawa, *Talanta*, **23**, 669 (1976).
2) R. Přibil, *Talanta*, **3**, 91 (1959).
3) G. Nakagawa and H. Wada, *Talanta*, **20**, 829 (1973).
4) G. Nakagawa and H. Wada, *Talanta*, **22**, 563 (1975).
5) J. Körbl and R. Přibil, *Chem. Ind. (London)*, **1957**, 233.
6) M. Murakami, T. Yoshino, and S. Harasawa, *Talanta*, **14**, 1293 (1967).