Kinetics of the Ligand Substitution Reactions of the Copper(II) Chelates of 1-(2-Pyridylazo)-2-naphthol Analogs with EDTA

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The rates of the substitution reactions of copper(II) chelates of metallochromic indicators such as 1-(2-pyridylazo)-2-naphthol (PAN, Hpan), 1-(2-thiazolylazo)-2-naphthol (TAN, Htan), 2-(2-pyridylazo)-4-methylphenol (PAC, Hpac), 2-(2-thiazolylazo)-4-methylphenol (TAC, Htac), 4-(2-pyridylazo)resorsinol (PAR, H_2par), and 4-(2-thiazolylazo)resorcinol (TAR, H_2tar) were determined. The rate laws can be written as $-\frac{d[CuL]}{dt}=k^{CuL}_{edta'}[CuL][edta']$ for PAN, TAN, PAC, and TAC in the pH range of 4 to 6.5, and $-\frac{d[(CuL)']}{dt}=(k^{CuL}_{edta'}[CuL]+k^{CuHL}_{edta'}[CuHL])[edta']$, where $[(CuL)']=[CuL]+[CuHL]$, for PAR and TAR in the pH range of 3.5 to 6.5. In the pH range lower than 3.5 the laws are written as $-\frac{d[CuL]}{dt}=(k^{CuL}_{edta'}[edta']+k^{CuL}_{H}[H])[CuL]$ for PAN, and as $-\frac{d[CuHL]}{dt}=(k^{CuHL}_{edta'}[edta']+k^{CuHL}_{H}[H])$ [CuHL] for PAR and TAR. The rate constants ($\mu=0.1$, 25 °C, dioxane 2 vol% or 5 vol% (PAN and TAN) ($dm^3\ mol^{-1}\ s^{-1}$)) are $k^{Cu(tan)}_{edta'}=2.8\times10^4$, $k^{Cu(pac)}_{edta'}=8.0\times10^4$, $k^{Cu(tac)}_{edta'}=4\times10^6$, $k^{Cu(par)}_{edta'}=2.0\times10^3$, $k^{Cu(tar)}_{edta'}=6.3\times10^4$, $k^{Cu(Hpar)}_{edta'}=1.2\times10^4$, $k^{Cu(Htar)}_{edta'}=7.9\times10^5$, $k^{Cu(pan)}_{H}=6.5\times10$, $k^{Cu(Hpar)}_{H}=6.6\times10^2$, and $k^{Cu(Htar)}_{H}=1.2\times10^4$. The rate constants, $k^{CuL}_{edta'}$, are inversely proportional to the basicities of the donor atoms of indicators. Thus, the rate of color change of thiazolylazo compound is larger than that of corresponding pyridylazo compound in the chelatometry of copper(II).

In the chelatometric titrations using metallochromic indicators, the rate of substitution reaction of the metal-indicator chelate with EDTA is one of the important factor in obtaining the sharp color change at the equivalence point.[1] Several papers have been published on the substitution reactions of metallochromic indicator chelates with complexans. The mechanisms of the substitution reactions of some metal chelates of 4-(2-pyridylazo)resorcinol with 1,2-bis(2-aminoethoxy)-ethane-*N*,*N*,*N'*,*N'*-tetraacetic acid or 1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid have been elucidated by Tanaka and Funahashi.[2-4] In our previous work, the kinetics of the substitution reaction of copper(II)-1-(2-pyridylazo)-2-naphthol(PAN) chelate with EDTA was investigated.[5] The structure of indicator influences the rate of the color change in the chelatometric titrations. In the case of heterocyclic azophenols, the rate of color change of a pyridylazophenol indicator is slower than that of a thiazolylazophenol indicator. For example the rate of color change of 4-(2-pyridylazo)resorcinol is smaller than that of 4-(2-thiazolylazo)resorcinol in copper(II)-EDTA titrations.

In this work the rates of the substitution reactions of copper(II) chelates of the several 1-(2-pyridylazo)-2-naphthol derivatives with EDTA have been determined, and the reaction mechanisms and the influences of the indicator structure on the rate of the substitution reaction are discussed.

Experimental

Reagents. Copper(II) nitrate solution: Copper metal (99.99%) was dissolved in dilute nitric acid. Indicator solutions: TAN, PAC, TAC, PAR, and TAR synthesized and/or purified as described in previous papers[6-9] were dissolved in dioxane. Commercial $Na_2H_2edta\cdot2H_2O$ was recrystallized. Dioxane was purified as described in the previous paper.[5] Buffers: 0.1 mol dm^{-3} $ClCH_2COOH$–$ClCH_2COOK$ (pH<4.5), and 0.1 mol dm^{-3} 2-morpholino-1-ethanesulfonicacid(MES)–KOH (pH 4.5—7) were used. Ionic strength was maintained at 0.1 with KNO_3. All experiments were carried out in 2 or 5 vol % dioxane–H_2O solutions at (25±1) °C.

Apparatus. A Union Giken Stopped-Flow Spectrophotometer Type RA-401 (dead time 3 ms), a Hitachi Rapid Scan Spectrophotometer Type TSP-2 (dead time 20 ms), and a Radiometer pH Meter Type 26 were used.

Results

Substitution Reactions of Copper(II) Chelates of TAN, PAC, and TAC with EDTA. When a small excess of the indicator compared with copper(II) ion is added, these indicators form the 1:1 chelates with copper(II) at pH values lower than 6.5. The rate of the substitution reaction of indicator chelate, CuL, with a large excess of EDTA was determined under the experimental conditions shown in Table 1. The rate law is expressed as (Charges are omitted for simplicity.)

$$-\frac{d[CuL]}{dt}=k_{obsd}[CuL], \qquad (1)$$

where k_{obsd} is the conditional rate constant.[5] Decrease in the absorbance of CuL chelate was measured as a function of the reaction time. The pseudo first-order plots were obtained for at least 90% of the total reaction. In every case k_{obsd} was proportional to the total concentration of EDTA not combined with copper(II), [edta'], while no dependence on the concentration of excess indicator and hydrogen ion concentration was observed, the same result as in the case of PAN.[5] Hence the rate law can be written as

$$-\frac{d[CuL]}{dt}=k^{CuL}_{edta'}[edta'][CuL]. \qquad (2)$$

TABLE 1. EXPERIMENTAL CONDITIONS EMPLOYED FOR THE DETERMINATION OF THE RATE CONSTANTS

	Wavelength nm	10^6C_{Cu} mol dm^{-3}	10^5C_{L} mol dm^{-3}	10^4C_{EDTA} mol dm^{-3}	pH range	Dioxane vol%
PAN	550	5.0	0.5 —1.5	1.0 —2.0	2.5—5	5
TAN	575	4.0	0.48—0.78	0.40—1.0	4.5—5.2	5
PAC	570	10.0	1.5 —3.0	1.0 —1.4	4.4—5.1	2
TAC	605	5.0	0.75—1.5	0.50	4.0—4.6	2
PAR	542	10.0	1.5 —3.0	1.0 —2.0	2.8—6.5	2
TAR	557	10.0	1.5	1.0 —5.0	2.5—6.5	2

The rate constants obtained are summarized in Table 2.

In the case of TAC, since the substitution reaction was too fast to be measured accurately on the stopped-flow apparatus employed in this work, the value of the rate constant was roughly estimated.

Substitution Reactions of Copper(II) Chelates of PAR, and TAR with EDTA. In the cases of PAR and TAR, copper(II) forms a chelate, CuHL, with PAR at pH<4 and with TAR at pH<3.5. The protonation constants, $K^{\mathrm{H}}_{\mathrm{CuHL}}$, had been determined as $10^{5.07}$ for PAR[8] and $10^{4.37}$ for TAR[6] (dioxane 2 vol%, $\mu=0.1$, 15 °C). The absorption maxima of Cu(Hpar) and Cu(par) are at 525 and 515 nm, respectively, and the isosbestic points appear at 440 and 542 nm. The absorption maxima of Cu(Htar) and Cu(tar) are at 560 and 520 nm, respectively, and the isosbestic points appear at 450 and 557 nm. The rates of the substitutions of copper(II) chelates of PAR or TAR with large excess of EDTA were determined in the pH range from 2.5 to 6.5 by measuring the decrease in the absorbance of the chelates at an isosbestic point as a function of reaction time under the conditions shown in Table 1.

To examine the influence of buffer, in the pH range from 3 to 4.5 both $\mathrm{ClCH_2COOH}$–$\mathrm{ClCH_2COOK}$ buffer and MES–KOH buffer were used. No difference in the rate of the reactions was observed.

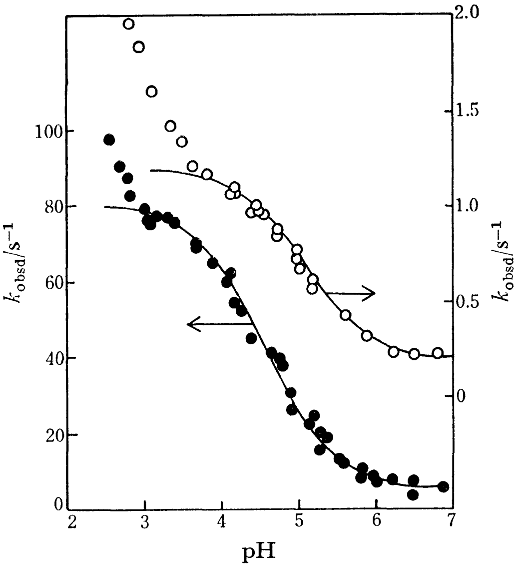

Fig. 1. Plots of k_{obsd} *vs.* pH for PAR and TAR.
○: PAR, ●: TAR.
k_{obsd} obtained at various concentrations of EDTA were converted to the values at 1.0×10^{-4} mol dm^{-3} C_{EDTA}. The lines are the theoretical curves calculated with the values obtained by curve fitting.

As seen from Fig. 1, the marked increases in the rates of the substitution reactions were observed with decreasing pH between pH 3.5 and 6. At the various pH values the conditional rate constants, k_{obsd}, were proportional to the concentration of EDTA, but independent of the concentration of PAR or TAR. As described above, the protonation equilibrium,

$$\mathrm{CuL} + \mathrm{H}^+ \rightleftharpoons \mathrm{CuHL}, \tag{3}$$

exists in the pH range from 4 to 6 for PAR or from 3.5 to 5.5 for TAR. Thus, the substitution reaction proceeds as

$$\begin{array}{l} \mathrm{CuL} + \mathrm{edta}' \rightleftharpoons \mathrm{Cu(edta)} + \mathrm{L}' \qquad (4) \\ \Big\updownarrow \mathrm{H}^+ \\ \mathrm{CuHL} + \mathrm{edta}' \rightleftharpoons (\mathrm{Cuedta})' + \mathrm{L}'. \qquad (5) \end{array}$$

If the total concentration of CuHL and CuL is expressed as [(CuL)′], the rate law is given by

$$\begin{aligned} -\frac{\mathrm{d}[(\mathrm{CuL})']}{\mathrm{d}t} &= k_{\mathrm{obsd}}[(\mathrm{CuL})'] \\ &= (k^{\mathrm{CuL}}_{\mathrm{edta}'}[\mathrm{CuL}] + k^{\mathrm{CuHL}}_{\mathrm{edta}'}[\mathrm{CuHL}])[\mathrm{edta}'] \\ &= \left(k^{\mathrm{CuHL}}_{\mathrm{edta}'} + \frac{k^{\mathrm{CuL}}_{\mathrm{edta}'} - k^{\mathrm{CuHL}}_{\mathrm{edta}'}}{1+K^{\mathrm{H}}_{\mathrm{CuHL}}[\mathrm{H}]}\right)[(\mathrm{CuL})'][\mathrm{edta}'], \end{aligned} \tag{6}$$

where

$$K^{\mathrm{H}}_{\mathrm{CuHL}} = \frac{[\mathrm{CuHL}]}{[\mathrm{CuL}][\mathrm{H}]}. \tag{7}$$

The plot of k_{obsd} *vs.* pH in each case was compared with a family of normalized functions $y=p/(1+x)=f(\log x)$. As shown in Fig. 1, the plot fits well one of the theoretical curves. The values of $k^{\mathrm{CuL}}_{\mathrm{edta}'}$, and $k^{\mathrm{CuHL}}_{\mathrm{edta}'}$ are listed in Table 2.

As seen in Fig. 1 the rate of substitution reaction of CuHL further increased at pH values lower than 3.5 for PAR and 3.0 for TAR. In these pH ranges Cu-

TABLE 2. RATE CONSTANTS OF SUBSITUTION REACTIONS OF Cu(II) CHELATES WITH EDTA AT $\mu=0.1$, AT 25 °C

	$k^{\mathrm{CuL}}_{\mathrm{edta}'}$ or $k^{\mathrm{CuHL}}_{\mathrm{edta}'}$ dm^3 mol^{-1} s^{-1}	$k^{\mathrm{CuL}}_{\mathrm{H}}$ or $k^{\mathrm{CuHL}}_{\mathrm{H}}$ dm^3 mol^{-1} s^{-1}
Cu(pan)	1.9×10^3	6.5×10
Cu(tan)	2.8×10^4	
Cu(pac)	8.0×10^4	
Cu(tac)	4×10^6	
Cu(par)	2.0×10^3	
Cu(Hpar)	1.2×10^4	6.6×10^2
Cu(tar)	6.3×10^4	
Cu(Htar)	7.9×10^5	1.2×10^4

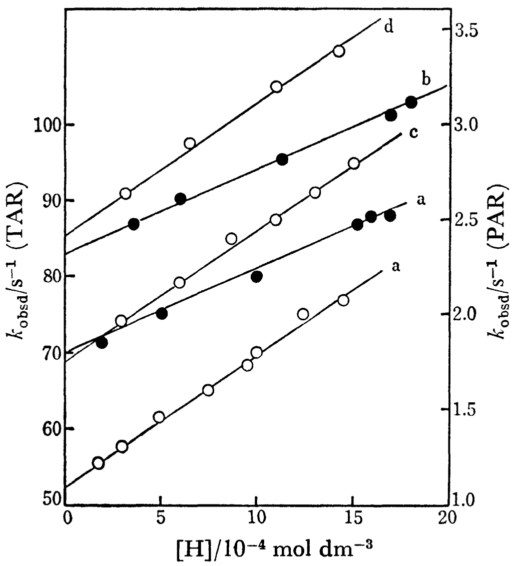

Fig. 2. Plots of log k_{obsd} *vs.* [H].
○: PAR, ●: TAR.
$C_{EDTA}=1.0\times10^{-4}$ (a), 1.2×10^{-4} (b), 1.5×10^{-4} (c), 2.0×10^{-4} mol dm^{-3} (d).

(Hpar) or Cu(Htar) is predominantly formed. Plots of k_{obsd} *vs.* the concentration of hydrogen ion yielded straight lines with intercepts on the y-axes. (Fig. 2). Thus the rate law can be expressed as

$$-\frac{d[CuHL]}{dt} = (k^{CuHL}_{edta'}[edta']+k^{CuHL}_{H}[H])[CuHL]. \qquad (8)$$

The values of $k^{CuHL}_{edta'}$ and k^{CuHL}_{H} were obtained from the intercepts and the slopes of the straight lines, respectively:

$$k^{Cu(Hpar)}_{edta'} = 1.1\times10^{4}\ dm^{3}\ mol^{-1}\ s^{-1},$$
$$k^{Cu(Htar)}_{edta'} = 7.0\times10^{5}\ dm^{3}\ mol^{-1}\ s^{-1},$$
$$k^{Cu(Hpar)}_{H} = 6.6\times10^{2}\ dm^{3}\ mol^{-1}\ s^{-1},$$
$$k^{Cu(Htar)}_{H} = 1.2\times10^{4}\ dm^{3}\ mol^{-1}\ s^{-1}.$$

The values of $k^{CuHL}_{edta'}$ obtained were approximately equal to the values previously obtained by the curve fitting method.

Substitution Reaction of Copper(II) Chelate of PAN with EDTA. In our previous work,[5] the rate of the substitution reaction of Cu(pan) with EDTA was determined in the pH range from 5.0 to 6.3, in which PAN can be used as an indicator for the chelatometric titrations of copper(II). In this pH range, the substitution reaction is of first-order with respect to EDTA and Cu(pan), while there is no dependence on pH as in the cases of TAN, PAC, and TAC. In this study, in the lower pH range the rate of the substitution reaction of Cu(pan) with EDTA was examined. At pH lower than 4 the rate of the reaction gradually increased with decreasing pH, as in the cases of PAR and TAR. The conditional rate constants, k_{obsd}, depended on [H] and [edta'], hence the rate law can be written as

$$-\frac{d[Cu(pan)]}{dt} = (k^{Cu(pan)}_{edta'}[edta']+k^{Cu(pan)}_{H}[H])[Cu(pan)]. \qquad (9)$$

The values of $k^{Cu(pan)}_{edta'}$ and $k^{Cu(pan)}_{H}$ obtained are shown in Table 2. The values of $k^{Cu(pan)}_{edta'}$ determined in this study agrees with that obtained in the previous study:[5]

$$k^{Cu(pan)}_{edta'} = 1.7\times10^{3}\ dm^{3}\ mol^{-1}\ s^{-1}.$$

Discussion

The constant rates were observed in the following pH ranges: pH 3.5—6.3 for Cu(pan), pH 4.5—5.2 for Cu(tan), pH 4.4—5.1 for Cu(pac), pH 4.0—4.6 for Cu(tac), pH 6—6.5 for Cu(par) and for Cu(tar), while the fraction of H_2edta, Hedta, and edta changes in these pH ranges. Cassatt and Wilkins reported that in the reaction of EDTA with nickel(II) ion Hedta is 10^2-fold more reactive than H_2edta.[10] From our results, however, no difference in the rate of substitution reaction with different protonated forms of EDTA was observed. Copper(II) chelates, CuL, of PAN, TAN, PAC, TAC, PAR, and TAR are substituted by EDTA in these pH regions according to the following mechanism, as proposed by Tanaka and Funahashi:

$$\mathrm{CuL} + \mathrm{edta'} \rightleftarrows \mathrm{CuL(edta)} \xrightarrow{\text{r.d.s.}} \mathrm{Cu(edta)} + \mathrm{L'}. \qquad (10)$$

The values of log $k^{CuL}_{edta'}$ were plotted against the sum of the dissociation constants of protonated pyridine or thiazole and phenolic *o*-hydroxyl groups ($pk_{NH}+pk_{o\text{-}OH}$). (Fig. 3). A straight line was obtained. This result indicates that the rate of the substitution reaction of CuL chelate is inversely proportional to the basicities of the donor atoms of the leaving ligands. However, the values of log $k^{CuL}_{edta'}$ for Cu(pan) and Cu(tan) chelates are smaller than those of other indicators, probably due to the steric effect of the naphthalene ring in PAN or TAN. Since the basicities of donor atoms in the thiazolylazo compounds are weaker than those of corresponding pyridylazo compounds, the rate of the substitution reaction of copper(II) chelates of thiazolylazo compounds is, generally speaking, faster than that of corresponding pyridylazo compound chelates. Thus, as regards the rate of color change, the thiazolylazo compounds are more favorable for use as metallochromic indicators than the pyridylazo compounds.

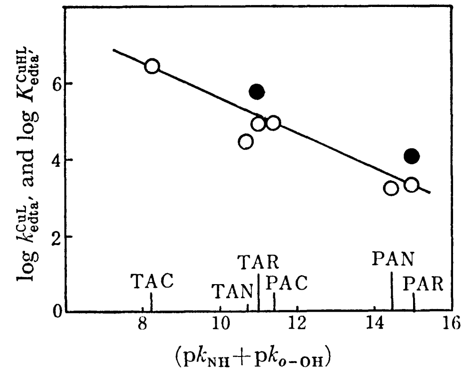

Fig. 3. Plots of log $k^{CuL}_{edta'}$, and log $K^{CuHL}_{edta'}$ *vs.* ($pk_{NH}+pk_{o\text{-}OH}$).
○: $k^{CuL}_{edta'}$, ●: $K^{CuHL}_{edta'}$.

The reaction rate of CuHL chelate with PAR or TAR is faster than that of CuL by one order. In the chelatometric titrations of copper(II) with EDTA using TAR as an indicator, the optimum pH range is from 4 to 6. The large rate of the substitution reaction of Cu(Htar) chelate with EDTA gives a great advantage for the sharp color change of the indicator at the equivalence point.

References

1) G. Nakagawa and H. Wada, *Talanta*, **20**, 829 (1973).

2) M. Tanaka, S. Funahashi, and K. Shirai, *Inorg. Chem.*, **7**, 573 (1968).

3) S. Funahashi, S. Yamada, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **43**, 769 (1970).

4) S. Funahashi, M. Tabata, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **44**, 1586 (1971).

5) G. Nakagawa and H. Wada, *Talanta*, **22**, 563 (1975).

6) H. Wada and G. Nakagawa, *Bunseki Kagaku*, **14**, 28 (1965).

7) G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **83**, 1098 (1962).

8) H. Wada and G. Nakagawa, *Nippon Kagaku Zasshi*, **85**, 549 (1964).

9) G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **85**, 202 (1964).

10) J. C. Cassatt and R. G. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).