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Mechanism of the Acceleration Effect of 1,10-Phenanthroline on the Rate of Color Change of Xylenol Orange in the Chelatometric Titration of Nickel(II)

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Synopsis. The effect in the title was studied kinetically. Experimental results indicate that the color change reaction in the presence of 1,10-phenanthroline proceeds according to a mechanism proposed by Nakagawa and Wada.

It is essential for a metallochromic indicator to be released rapidly from the metal-indicator complex at the equivalence point in the chelatometric titration of the metal. The lack of this property causes a sluggish color change at the equivalence point, and introduces a titration error.

Because Xylenol Orange (XO) forms an inert complex with copper(II) or nickel(II), its color change is slow in direct titrations of these metals with EDTA. Pribil observed that the rate of the XO color change was markedly improved by addition of a small amount of 1,10-phenanthroline (phen) in the titration of copper.1) He explained this effect by supposing a reaction scheme comprised of two rapid substitution reactions:

$$\mathrm{MI} + \mathrm{X} = \mathrm{MX} + \mathrm{I} \qquad (1)$$

$$\mathrm{MX} + \mathrm{Y} = \mathrm{MY} + \mathrm{X} \qquad (2)$$

where M is the metal ion, I the indicator, X an auxiliary complex-forming agent (namely, phen in this case), and Y a chelatometric titrant (namely, EDTA in this case).

Recently Nakagawa and Wada published results of an extensive study on effects of auxiliary complex-forming agents on the rate of color change of metallochromic indicators, and criticized Pribil's explanation on the ground of the smallness of the stability constant difference between copper-XO and copper-phen complexes.2) They proposed another reaction scheme involving a mixed ligand complex.

$$\mathrm{MI} + \mathrm{X} = \mathrm{MIX} \qquad (3)$$

$$\mathrm{MIX} + \mathrm{Y} = \mathrm{MY} + \mathrm{I} + \mathrm{X} \qquad (4)$$

They, however, did not supply any kinetic data supporting this scheme.

The purpose of the present study is to examine the two schemes kinetically in the case of the titration of nickel(II).

Experimental

All chemicals used were of reagent grade, and all solutions were prepared with redistilled water. A standard solution of disodium salt of EDTA and stock solutions of XO and phen were prepared by dissolving weighed amounts. The concentration of nickel sulfate solution was determined by titration with the standard solution of EDTA, where murexide was used as indicator.3) Acetate buffers of pH 4.54 to 5.33 were used for the control of hydrogen ion concentration of the reaction mixtures.

A solution of 50 ml was prepared by mixing nickel sulfate, XO, phen, an acetate buffer, and EDTA of insufficient amount to be equivalent to the amount of nickel sulfate, and by filling to the mark with water. The concentration of nickel sulfate was prepared to be 5.00_0 mM, and the ionic strength of the solution was controlled to 0.2. The solution, in a measuring flask, was placed in a thermostat kept at 25 °C. After equilibration a meaured volume (0.17 to 0.46 ml) of the EDTA solution was added to the solution to make the concentration of EDTA to be 1% excess of nickel sulfate. This was rapidly followed by thorough mixing and transfer of the solution into a quartz cell with light path of 10 mm. The change of transmittance of the solution with time was followed by a Hitachi Model 101 spectrophotometer, its cell compartment being kept at 25.0 °C. The transimittance was measured at 582 nm, where the nickel-XO complex showed an absorption peak and the free XO did not absorb to any appreciable degree.

Results and Discussion

The rate of the substitution reaction of the nickel-XO complex with EDTA follows the second-order rate law both in the presence and in the absence of phen, as shown in Fig. 1, where a and b are the initial concentrations of the nickel-XO complex and EDTA, respectively, and $(a—x)$ and $(b—x)$ are the concentrations of the respective species at time t.* Although the rate constant in the presence of phen, k_1, and that in the absence of phen, k_2, were both susceptible to the influence of con-

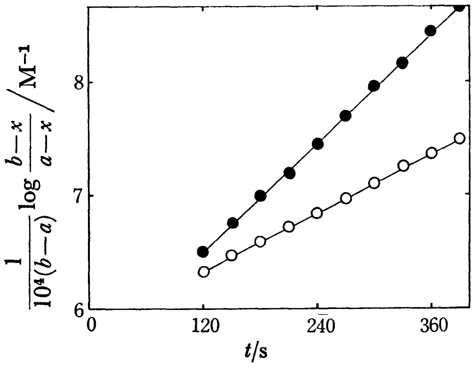

Fig. 1. Second-order rate plots of the substitution reaction of the nickel-XO complex with EDTA. pH of reaction mixtures, 4.92. Concentration of XO, 5.0 μM. Concentration of EDTA added just at the start, $20._0$ μM. Concentration of phen: ○, 0 μM; ●, 1.0 μM.

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* XO, EDTA, and phen in solutions can exist in forms with different numbers of protons. Concentrations of these species were calculated, however, irrespective of the number of protons because the concentration of hydrogen ions had no influence on (k_1-k_2), about which we are concerned.

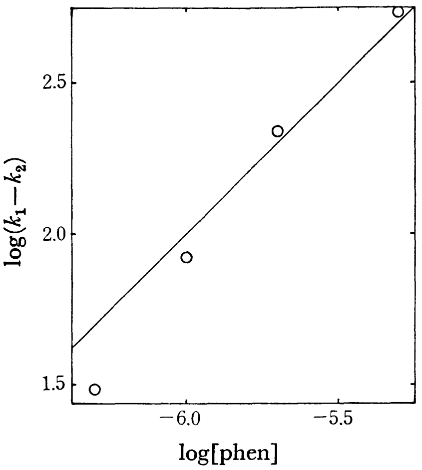

Fig. 2. Dependence of log (k_1-k_2) on log[phen]. The solid line is a straight line with a slope of 1. Units of [phen] and (k_1-k_2) are M and M^{-1} s^{-1}, respectively. pH of reaction mixtures, 4.92. Concentration of XO, 5.0 μM. Concentration of EDTA added just at the start, $30._0$ μM.

centrations of hydrogen ions and XO, the difference $(k_1—k_2)$ was not. This difference, representing the acceleration effect of phen, varies with the first power of the concentration of phen, as shown in Fig. 2.

In Pribil's scheme the rate-determining step may be either Reaction (1) or (2). Neither case leads to the second-order rate law described above. Nakagawa-Wada's scheme, on the other hand, can satisfy this rate law if Reaction (6) is the rate-determing step as given by

$$\mathrm{MI} + \mathrm{X} \overset{K}{\rightleftharpoons} \mathrm{MIX} \qquad (5)$$

$$\mathrm{MIX} + \mathrm{Y} \xrightarrow{k} \mathrm{MY} + \mathrm{I} + \mathrm{X} \qquad (6)$$

and if the equilibrium constant K is so small as to fulfill the relation $[\mathrm{X}] \gg [\mathrm{MIX}]$. Under these conditions the rate is written as

$$\text{rate} = kK[\mathrm{X}][\mathrm{MI}][\mathrm{Y}] \qquad (7)$$

which agrees with experimental observations. Hence Nakagawa-Wada's mechanism works in the case of titration of nickel(II).

References

1) R. Pribil, *Talanta*, **3**, 91 (1959).
2) G. Nakagawa and H. Wada, *ibid.*, **20**, 829 (1973).
3) G. Schwarzenbach, "Complexometric Titrations," Methuen, London (1957), p. 80.