

THE KINETICS OF THE REACTION BETWEEN NICKEL(II) TETRAETHYLENEPENTAMINE AND TRIETHYLENETETRAMINEHEXAACETATE IONS

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The kinetics of the ligand-ligand substitution reaction between nickel(II) tetraethylenepentamine and triethylenetetraminehexaacetate has been studied. Using the cyanide quenching technique it was found that the reaction is first order with respect to tetraethylenepentamine Ni(II) ion and first order with respect to triethylenetetraminehexaacetate. The reaction mechanism is similar to the mechanism of the reaction between EDTA and tetraethylenepentamine Ni(II) ion. The reaction studied is faster than other similar reactions of EDTA and it proceeds in the presence of an excess of tetraethylenepentamine Ni(II) ion, the reaction product is a mixture of mono- and binuclear nickel(II) triethylenetetraminehexaacetate chelates and the corresponding mechanism is more complex.

The kinetics and mechanism of substitution reactions involving multidentate ligands and transition metal ions have been studied¹⁻⁴. Great interest has been paid to the kinetics of the reactions of the complexes of EDTA and related ligands. In this work, the results of a study connected with the ligand-ligand substitution reaction between nickel(II) tetraethylenepentamine (B) and triethylenetetraminehexaacetate (H₆L) ions are presented. The displacement of polyamines from their Ni(II) complexes by EDTA was studied by Rorabacher and Margerum⁵, and it has been found that the corresponding reaction mechanism involved a series of mixed ligand intermediates.

EXPERIMENTAL

Reagents and apparatus. All the solutions used were prepared from reagent grade chemicals. Solutions of Ni(ClO₄)₂ were standardized by EDTA titration. Solutions of triethylenetetraminehexaacetic acid (H₆L) were prepared from the product of Dojin Pharmaceutical Laboratories (Japan), the pH of the resulting solution was adjusted approx. to 7, and the solution was standardized by amperometric titration with a Ni(II) ions solution. Tetraethylenepentamine (Fluka A.G., F.G.R.) was purified by recrystallization several times from ethanol-water solution⁶ and prepared as the NO₃⁻ salt. The NO₃⁻ salt was dissolved in water and the resulting solution was standardized spectrophotometrically with standard Cu(II) solution at 580 nm. The solution of NiB²⁺ was prepared by adding a slight excess of Ni(ClO₄)₂ to the amine solution and precipitating the excess Ni(II) ions by addition of NaOH to pH 11.5. After filtration, the pH was

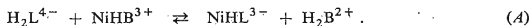
adjusted to approx. 7.0. The concentration of Ni(II) in this solution was checked by adding an excess of cyanide ions at pH 10 and measuring the concentration of the $[\text{Ni}(\text{CN})_4]^{2-}$ formed⁷. Solutions of 0.025M boric acid and sodium borate were used as buffer solutions in the pH region 5.5–9.5. The ionic strength of the measured solution was maintained constant at 0.1 with reagent grade sodium perchlorate. Spectrophotometric measurements were carried out with the ultraviolet spectrophotometer Unicam SP 800 (Unicam Instr., England) with a thermostated cell compartment. pH values of the solution examined were measured with the Radiometer PHM-25, (Copenhagen, Denmark).

Procedure. The determination of the concentration of NiB^{2+} during its reaction with H_6L was based on the differences of the reaction rates of NiL^{4-} and NiB^{2+} complexes with cyanide ions. The products of both these reactions are $[\text{Ni}(\text{CN})_4]^{2-}$ ions and the concentration of $[\text{Ni}(\text{CN})_4]^{2-}$ can be determined spectrophotometrically at 268 nm. The reaction of NiB^{2+} with cyanide ions is fast⁵, while the reaction of the NiL^{4-} complexes is relatively slow⁸. This fact enabled use of a quenching method for the determination of the amount of NiB^{2+} in the presence of NiL^{4-} . The test experiments showed that when the spectrophotometric measurement was carried out in a time interval of 5 min after the addition of cyanide to the mixture of both Ni(II) complexes, all the NiB^{2+} was converted to $[\text{Ni}(\text{CN})_4]^{2-}$ while the NiL^{4-} chelate remained unchanged. The method was verified by the addition of a mixture of cyanide and H_6L to the solution of NiB^{2+} . The results of the spectrophotometric measurement again showed that all the nickel(II) was converted to $[\text{Ni}(\text{CN})_4]^{2-}$ immediately. The measurements of the reaction rates were carried out as follows: The reaction mixture $\text{NiB}^{2+} + \text{H}_6\text{L}$ was prepared under given conditions (pH, ionic strength). To a portion of this solution, a ten times molar excess of sodium cyanide (calculated with respect to the amount of Ni(II)) and NaOH were added and the absorbance of the resulting $[\text{Ni}(\text{CN})_4]^{2-}$ complex was measured at 268 nm not later than 5 min after mixing. The determined concentration of $[\text{Ni}(\text{CN})_4]^{2-}$ corresponded to the concentration of NiB^{2+} .

RESULTS

Kinetics Measurements in the System Containing H_6L and NiB^{2+}

For the measurement of the reaction rates the method of cyanide quenching was used. In the pH interval between 7–8 the reaction system may be formulated by the equation



For the determination of the reaction order the method of initial rates was applied. Measurements were carried out with a constant concentration of H_6L and a varying concentration of NiB^{2+} , and with a constant concentration of NiB^{2+} and a varying concentration of H_6L . The results showed that the reaction studied is first order with respect to H_6L and first order with respect to NiB^{2+} . The rate equation was therefore formulated as:

$$-d[\text{NiB}^{2+}]/dt = k_1'[\text{NiB}^{2+}]' [\text{L}^{6-}]', \quad (I)$$

where the terms $[\text{NiB}^{2+}]'$ and $[\text{L}^{6-}]'$ include all protonated and unprotonated forms of NiB^{2+} and H_6L .

Further experiments, carried out with the concentration of NiB^{2+} equal to the concentration of H_6L , gave a linear dependence of $1/[\text{NiB}^{2+}]'$ on time. The second order rate plots were linear for over 80% of the reaction time and passed through the theoretical intercept. The rate constants calculated from these plots for various pH values are summarized in Table I, from which it fol-

lows that the reaction rate decreases rapidly with increasing pH of the studied solutions. With respect to the dissociation of H_6L , the following rate equation was proposed

$$-d[NiB^{2+}]'/dt = \{k_L + k_{HL}[H^+] + k_{H_2L}[H^+]^2 + \dots + k_{H_6L}[H^+]^6\} [L^{-6}] [NiB^{2+}], \quad (2)$$

where the terms $k_L, k_{HL}, etc.$ are the rate constant of the corresponding protonated H_6L species. Because the rate measurements were carried out at $pH > 6$, the concentration of H_6L species involving three and more protons was negligible. Eq. (2) was therefore simplified to

$$\begin{aligned} -d[NiB^{2+}]'/dt &= \{k_L + k_{HL}[H^+] + k_{H_2L}[H^+]^2\} [L^{6-}] [NiB^{2+}] = \\ &= k'_L [NiB^{2+}]' [L^{6-}]'. \end{aligned} \quad (3)$$

On rearranging Eq. (3) following expression was obtained:

$$k'_L [NiB^{2+}]' [L^{6-}]' / [NiB^{2+}] [L^{6-}] = k_L + k_{HL}[H^+] + k_{H_2L}[H^+]^2. \quad (4)$$

In this expression the ratio $[L^{6-}]' / [L^{6-}]$ is defined by the equation

$$\begin{aligned} [L^{6-}]' / [L^{6-}] &= 1 + [H^+] / K_1 + [H^+]^2 / K_1 K_2 + [H^+]^3 / K_1 K_2 K_3 + \dots \\ &\dots + [H^+]^6 / K_1 K_2 K_3 K_4 K_5 K_6, \end{aligned} \quad (5)$$

where $K_1 - K_6$ are the dissociation constants of H_6L . The ratio $[NiB^{2+}]' / [NiB^{2+}]$ is defined by the equation

$$[NiB^{2+}]' / [NiB^{2+}] = 1 + [H^+] K_{NiHB}, \quad (6)$$

where K_{NiHB} is the protonation constant⁹ of $NiHB$ ($\log K_{NiHB} = 4.9$).

According to Eq. (4) a plot of $k'_L [NiB^{2+}]' [L^{6-}]' / [NiB^{2+}] [L^{6-}] = k'_L R$ vs $[H^+]$ should describe a parabolic relationship. This dependence is presented in Fig. 1, curve 1 and was tested by a plot of $[H^+]$ vs $k'_L R - (k'_L R)_1 / [H^+] - ([H^+])_1$. This plot yielded a straight line, which verified the parabolic nature of the studied dependence. Using the experimentally obtained data, the values of the constants k_L, k_{HL} and k_{H_2L} were calculated by solution of Eq. (4) for different values of $[H^+]$ and k_L . The calculated values were: $1.6 \cdot 10^3 \text{ mol}^{-1} \text{ s}^{-1}$, $6.0 \cdot 10^{10} \text{ mol}^{-2} \text{ s}^{-1}$

TABLE I

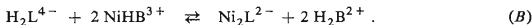
Rate Constants $\text{mol}^{-1} \text{ s}^{-1}$ for the Reaction between H_6L and NiB^{2+}
 $C_{H_6L} = C_{NiB} = 2.4 \cdot 10^{-5} \text{ M}$; $I = 0.1$; 22°C .

pH	$k'_L \cdot 10^{-4}$	pH	$k'_L \cdot 10^{-4}$	pH	$k'_L \cdot 10^{-4}$
6.50	1.30	7.50	0.41	8.15	0.10
6.80	1.18	7.70	0.22	8.40	0.09
7.10	0.62	8.05	0.15	8.70	0.08

and $1.6 \cdot 10^{17} \text{ mol}^{-3} \text{ s}^{-1}$ for k_L , k_{HL} and k_{H_2L} respectively. The solid curve (Fig. 1, curve 2), shows the calculated dependence of $k_L R$ on $[H^+]$ as predicted by Eq. (4).

Kinetic Measurements in the System Containing H_6L and an Excess of NiB^{2+}

Further experiments showed that all $Ni(II)$ was transferred from NiB^{2+} complex when the system studied contained H_6L reagent and a two-fold excess of NiB^{2+} . This finding led to the proposal that the binuclear nickel(II) chelate Ni_2L^{2-} was formed according to the reaction



The validity of reaction (B) was tested by experiments carried out with the total $Ni(II)$ concentration twice that of H_6L . The results showed that under these conditions all the NiB^{2+} disappeared from the system after a sufficient time interval. Similarly, the method of cyanide quenching was applied to measurement of the rate of reaction (B). The results showed the reaction to be second order. The plots of $1/[NiB^{2+}]$ vs time were linear up to about 50% reaction completion and passed through the theoretical intercepts. The reaction rate was found to depend on pH; it decreased with decreasing concentration of hydrogen ions. An attempt to interpret the dependence of the corresponding rate constant on pH, by the application of Eq. (4), failed, since the dependence was not parabolic (Fig. 1, curve 3).

DISCUSSION

A detailed study of the mechanism of the exchange reaction between EDTA and nickel(II) polyamines⁵ has shown that these reactions are of the same nature as the reaction of EDTA with aquonickel(II)-ions. It has been stated^{3,5} that the displacement of a polyamine coordinated to a $Ni(II)$ ion proceeds through a series of mixed ligand reaction intermediates. The intermediate prior to the rate determining step was found to have three amine nitrogens and one EDTA acetate bonded to the $Ni(II)$ ion; the remaining coordination sites are occupied by water molecules. The rate determining step is the loss of the water molecules followed by rapid bonding of the nitrogen donor atoms from the EDTA.

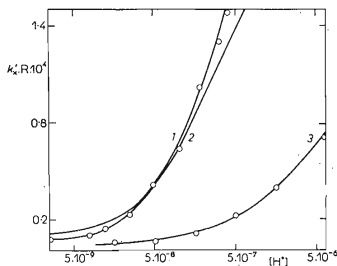


FIG. 1

Dependence of the Product $k'_L R$ on the Concentration of Hydrogen Ions

1 Experimental values k'_L ; 2 dependence calculated according Eq. (4); 3 as curve 1 measured in the system with an excess of NiB^{2+} (the total H_6L concentration equals half that of NiB^{2+}).

The reaction between H_6L and NiB^{2+} studied here is faster than the formation and dissociation rates of $Ni(II)$ -polyamine complexes⁹. This finding suggests that H_6L accelerates the removal of the amine group from the coordination sphere of $Ni(II)$. This, together with the structural similarity of H_6L and EDTA, led to the proposal that the removal of the amine group from the coordination sphere of $Ni(II)$ entails the formation of coordinate bonds between H_6L and the nickel(II) ion, prior to the complete dissociation of the amine group from the $Ni(II)$ ion. According to Rorabacher and Margerum⁵, an increasing number of similar donor atoms on the incoming ligand should increase the reaction rate. Because the H_6L molecule has ten donor atoms, an increase in the reaction rate could be expected when EDTA is replaced by H_6L in the reaction with the $Ni(II)$ amine complex. This phenomenon was actually observed: the value of the experimental rate constant k_Y^{NiB} for the exchange of EDTA with NiB^{2+} according to Rorabacher and coworkers⁵ is $1.5 \text{ mol}^{-1} \cdot \text{s}^{-1}$; the value of the constant, k_L^{NiB} , for the exchange of H_6L with BiN^{2+} found in the present paper is $1.6 \cdot 10^3 \text{ mol}^{-1} \text{ s}^{-1}$. The displacement of B by H_6L was found to proceed even under those conditions where the system studied contained an excess of NiB^{2+} . This process is formulated by reaction (B). The equilibrium constant of reaction (B), K_R , can be calculated using the equation

$$K_R = [Ni_2L^{2-}][H_2B^{2+}]^2/[H_2L^{4-}][NiHB^{3+}]^2 = \\ = K_{Ni_2L}(K_{H_2B}^H K_{HB}^H)^2/K_{H_2L}^H K_{HL}^H (K_{NiHB}^{NiB} K_{NiB})^2, \quad (7)$$

where K_{Ni_2L} , K_{NiB} and K_{NiHB}^{NiB} are the stability constants of the Ni_2L^{2-} , NiB^{2+} , and $NiHB^{3+}$ complexes respectively, and $K_{H_nL}^H$ and $K_{H_nB}^H$ are the corresponding acid dissociation constants of H_6L and B respectively. Because the values of all these constants are known, the value of $\log K_R$ was calculated and found to be equal to approx. 5. This finding suggests that the equilibrium expressed by reaction (B) is shifted to the right-hand side and the reverse reaction can therefore be neglected. The irregularities during the rate measurements carried out in the system containing an excess of NiB^{2+} however, showed the effect of the reverse reaction. This phenomenon is, most probably, due to the fact that the product of the reaction between H_6L and an excess of NiB^{2+} is a mixture of mono and binuclear chelates of $Ni(II)$ and H_6L and the corresponding reaction is more complex than shown by reaction (B). This proposal is in an agreement with the results of Harju¹⁰ who found that a 2 : 1 molar ratio mixture of $Ni(II)$ ions and H_6L contained solely the binuclear $Ni(II)$ chelate only at very low pH. The reaction system described by reaction (A) is, on the other hand, not influenced by the formation of Ni_2L , since reaction (B) is suppressed in alkaline solutions and under conditions when H_6L is in excess¹⁰ over $Ni(II)$.

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