Multidentate Ligand Substitution Kinetics: Reaction of Triethylenetetraminenickel(II) Complex with Diethylenetriaminepentaacetic Acid

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The kinetics of reactions of Ni(trien)\(^{2+}\) [triethylenetetraminenickel(II)] and DTPA\(^5\) (diethylenetriaminepentaacetic acid) has been studied spectrophotometrically at pH 5.5-11.0 (\(\ell=0.1\) mol dm\(^{-1}\)) and followed by the cyanide quenching method. The reaction is first order each in [Ni(trien)] and [DTPA]. The second order rate constants have been evaluated using initial rate method and confirmed by integrated second order rate plots. The pH dependence of the reaction has been interpreted in terms of reactivities of hydroxo species of nickel complex and protonated forms of DTPA\(^5\). A ten-step reaction mechanism proposed earlier [Indian J Chem, 19A (1981) 1070] for Ni(trien)\(^{2+}\)-HEEDTA reaction also holds good for the title reaction; slight increase in observed rate constant for DPTA reaction in comparison to HEEDTA reaction is attributable to an increase in the number of binding sites of the incoming DPTA. The rate-determining step involves loss of water molecule followed by coordination of nitrogen of the aminocarboxylate.

### Results and Discussion

The rate of exchange of DTPA with Ni-trien complex was studied as a function of [DTPA], [Ni(trien)]\(^{2+}\), pH and temperature. The rate of formation of Ni(DTPA) at constant pH is first order each with respect to [Ni(trien)]\(^{2+}\) and [DTPA]. The rate expression is:

\[
\frac{d[\text{Ni(trien)}]}{dt} = k_{T}^{\text{Ni-TR}}[\text{Ni(trien)}]\_T[D\text{TPA}]_T \quad \ldots(2)
\]

where [Ni(trien)]\(_T\) and [DTPA]\(_T\) represent all forms of Ni(trien) and DTPA respectively; \(k_{T}^{\text{Ni-TR}}\) (\(= 4.4 \times 10^2\) dm\(^3\)mol\(^{-1}\)s\(^{-1}\)) is the second order rate constant calculated by the initial rate method and confirmed by second order integrated rate plots. A slight deviation seen in integrated rate plots at longer reaction periods is due to the backward reaction.

The rate constants obtained in the temperature range 25-45°C were used to calculate activation parameters for the rate-determining step-3, given in a ten-step mechanistic scheme proposed by us earlier. \(E_a = 21 \pm 1\) kJ mol\(^{-1}\), \(\Delta S^* = -130 \pm 2\) JK\(^{-1}\) mol\(^{-1}\). The low positive value of \(E_a\) indicates an associative mechanism where bond formation and bond dissociation occur in a concerted manner.

The hydrogen ion dependence for the displacement of trien from its nickel complex by DTPA was studied between pH 5.5-11.0. The reaction rate decreases with increase in pH, attains a minimum value at pH 8, thereafter increases till pH 10 and then again decreases slightly.

This behaviour can be explained on the basis of the reactivities of various forms of DTPA and the stability constant of Ni(trien) complex (Eq. 3).
Rate = \( (k^{\text{NiT(OH)}}_L K^{\text{NiT(OH)}}_{\text{NiT}} \frac{K_w}{[H^+]}) + k^{\text{NiT}}_L \)

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_{\text{NiT}} K_{\text{NiT}} [H^+]^2 \]

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [H^+]^3 \]

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [L^-] \]  \( \text{(3)} \)

where \( K_1, K_2, K_3 \) are the first, second and third protonation constants of DTPA. (log \( K_1 = 10.55; \log \) \( K_2 = 8.60; \) and log \( K_3 = 4.26 \)) and \( K_w = |H^+| |OH^-| \).

In the pH range 5.5 to 6.5, DTPA is present mainly in the form of \( H_3L \) and \( H_2L \), so Eq. (3) assumes the form (4)

Rate = \( (k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [H^+]^2 \)

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [H^+]^3 \]

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [L^-] \]  \( \text{(4)} \)

Comparing Eq. (4) with Eq. (2) and dividing by \( [H^+]^2 \) we get

\[ k^{\text{NiT}}_L \frac{[\text{NiT}]}{[\text{NiT}]} [L] \frac{1}{[H^+]^3} = k^{\text{NiT}}_{\text{H}_2\text{O}} K_2 K_{\text{H}_2\text{O}} \]

\[ + k^{\text{NiT}}_{\text{H}_2\text{O}} K_3 K_{\text{H}_2\text{O}} [H^+] \]  \( \text{(5)} \)

From a plot of the left hand side of Eq. (5) versus \( [H^+] \) (Fig. la) the rate constants \( k^{\text{NiT}}_{\text{H}_2\text{O}} \) and \( k^{\text{NiT}}_L \) can be obtained. In the pH range 6.5 to 9.5 the rate equation can be written as

\[ A[H^+]^2 - \{k^{\text{NiT}}_{\text{NiT}} K_3 K_{\text{NiT}} [H^+] [H^+]^3 \}

\[ = k^{\text{NiT}}_{\text{H}_2\text{O}} K_2 K_{\text{H}_2\text{O}} [H^+] \]  \( \text{(6)} \)

where \( A \) is the left hand side of Eq. (5). \( k^{\text{NiT}}_{\text{NiT}} \) can be obtained from slope of plot of left hand side of Eq (6) versus \( [H^+] \) (Fig. 1b).

At pH above 9.5, the rate equation can be written as

\[ B - k^{\text{NiT}}_{\text{H}_2\text{O}} K_{\text{H}_2\text{O}} = k^{\text{NiT}}_L + k^{\text{NiT(OH)}}_L K^{\text{NiT(OH)}}_{\text{NiT}} K_w [H^+] \]  \( \text{(7)} \)

where \( B \) represents the left hand side of Eq (6).

The plot of left hand side of Eq (7) versus \([H^+]^{-1}\) (Fig. 1c) gives the values of \( k^{\text{NiT}}_L \) and \( k^{\text{NiT(OH)}}_L \). The resolved rate constants from Eqs (5-7) are given in Table I. The plot of \( \log k_{\text{NiT}} \) versus pH is given in Fig. 2. The solid line is calculated from the resolved rate constants and the relevant p\( K_a \)s. The agreement between calculated and experimental curve is reasonably good.

The kinetic behaviour of reaction intermediates in multidentate-multidentate substitution reactions can be estimated by comparing the relative rate constants observed with those calculated on the basis of proposed reaction mechanism. A consideration of the structural features of polyaminocarboxylates of nickel shows that during the formation of the first bond, a carboxylate donor group is highly favoured over a nitrogen donor due to their steric configuration and the hindered access of nitrogen to the nickel centre.
The entering group in the ligand substitution reaction facilitates the dissociation of the leaving group.

It is proposed, as was done earlier\(^5\)\(^\text{--7}\), that the entering aminocarboxylates form progressively increasing number of coordinate bonds with \(\text{Ni}^{2+}\) (while the nickel-polyamine bonds are ruptured in succession) prior to complete dissociation of the nickel-polyamine complex. In this way the aminocarboxylate, DTPA in this case, blocks the reformulation of the nickel-polyamine bond and acts in a way similar to protons in the dissociation reactions of nickel polyamides. A series of mixed-ligand complexes are formed, during the course of reaction, with entering and leaving groups. These features of such type of reactions have been given in a ten-step mechanistic scheme proposed by us earlier\(^5\) for \(\text{Ni(trien)}^{2+}\)-HEEDTA reaction.\(^6\)

From the foregoing discussion, it follows that the rate-determining step should be either the loss of \(\text{H}_2\text{O}\) molecule or the rupture of nickel-trien bond. The observed rate constants can be compared with the rate constants calculated for the rate-determining step on the basis of relative stability of intermediate preceding the rate-determining step using a procedure which was followed earlier\(^7\) and used for explaining the kinetic behaviour of \(\text{Ni(trien)}^{2+}\)-HEEDTA reaction\(^8\) and also for \(\text{Ni(Tetren)}^{2+}\)-TMDTA and \(\text{Ni(Tetren)}^{2+}\)-HEEDTA reaction systems\(^9\). According to this argument

\[
k_{\text{exp}} = k_n \cdot \frac{K_{\text{nth intermediate}}}{K_{\text{reactant}}} \quad \ldots (8)
\]

where

\[
K_{\text{nth intermediate}} = \frac{K_{\text{polyamine segment}} \cdot K_{\text{aminocarboxylate segment}}}{K_{\text{electrostatic}}}
\]

and \(k_n\) is the rate constant for the nickel-nitrogen or nickel-water bond rupture process. \(K_{\text{electrostatic}}\) has been estimated to be 0.1 (see ref. 6, 7).

The value of \(K_{\text{nth intermediate}}\) can be estimated and \(k_n\) assigned for a variety of possible choices of rate-determining steps and so a value for \(k_{\text{exp}}\) can be obtained for every step. Comparing these values of \(k = k_{\text{NiT}}^{\text{NiT}} = 3.8 \times 10^4 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ for step-3} \) with \(k_{\text{exp}} \) (\(= k_{\text{NiT}}^{\text{NiT}} = 6 \times 10^3 \text{dm}^3 \text{mol}^{-1} \text{sec}^{-1} \) obtained experimentally and given in Table 1) it can be concluded, as was done earlier by Rorabacher and Margerum\(^7\) and later by Nigam et al.\(^3\)^\(^\text{--6}\), that in all probability, the rate-determining step is the third one in a ten-step sequence\(^7\) where three nitrogens of trien and the acetate segment of aminocarboxylate are coordinated to \(\text{Ni}^{2+}\). The agreement in the case of HEEDTA \((k = k_{\text{NiT}}^{\text{NiT}} = 8.0 \times 10^2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})\) was much better\(^6\).

The increase in observed rate constant for DTPA reaction in comparison with the expected value may be attributed to an increase in the number of binding sites of the incoming ligand DTPA in comparison to that of HEEDTA\(^4\)^\(^\text{--10}\). This step involves the loss of a water molecule followed by coordination of the first nitrogen of aminocarboxylate.

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**References**