Kinetics & Mechanism of Complexation of Ni(II) by Pyridine-2-carboxylic Acid

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The experimental kinetic data of Voss and Jordan (J Am chem Soc. 98 (1976) 2713) for the reaction of Ni(II) with pyridine-2-carboxylic acid in the pH range 2.6-6.4 has been analysed and a new reaction scheme suggested. The calculated and experimental values of the overall rate constants show excellent agreement.

The formation of metal chelates is of great importance from biological and chemical view points. Therefore a comprehensive kinetic study of the complexation reaction would give information regarding the nature and properties of chelates.

The kinetics of reaction of nickel (II) with pyridine-2-carboxylic acid (L) was earlier investigated by Voss and Jordan1. They found that the kinetics of the reaction obeyed rate equation (1).

\[-d[Ni^{2+}]/dt = k_{obs}[Ni^{2+}][L]_T \] (1)

Based on the experimental data they suggested a mechanism (Scheme 1) in which ONH denotes the amino acid.

\[ \text{Scheme 1} \]

\[ k_{obs}K_1[H^+] = (k_{21} + k_{43}K_1[H^+]^{-1})k_{34}K_1^{+} \] (2)

The significant shortcoming of Scheme 1 was that the formation of the chelate from one of the intermediate species, i.e., MONH was not taken into consideration. Equation (2) could be simplified into two limiting equations (3) and (4) at low and high pHs, respectively.

\[ \log k_{obs}K_1[H^+] = \text{pH} + \log \frac{k_{43}k_{35}K_1}{k_{34}} \] (3)

\[ \log k_{obs}K_1[H^+] = \text{pH} + \log \frac{k_{43}k_{35}K_1}{(k_{34} + k_{35})} \] (4)

A plot between \( k_{obs}K_1[H^+]/[H^+] \) and pH gives the values of intercepts to be \( \log k_{12}k_{34}K_1/k_{34} \) and \( \log k_{12}k_{35}K_1/(k_{34} + k_{35}) \) at low and high pHs, respectively. We analysed the data of Voss and Jordan and based on their Scheme 1, calculated the values of the intercepts at low and high pHs. These results are presented in Table 1. It is found that there is no good agreement between experimental and calculated values. Therefore, it was thought desirable to modify the reaction scheme of Voss and Jordan so as to get a better agreement.

The best fit with the experimental observations is obtained, if Scheme 1 is modified by including the step rate constant \( k_{25} \) for the formation of the chelate from MONH as given in Scheme 2.

\[ \text{Scheme 2} \]

The overall rate at which Ni(II) and pyridine-2-carboxylic acid disappear is given by Eq. (5).

\[-d[Ni^{2+}]/dt = k_{obs}[Ni^{2+}][L]_T \] (5)

Hence,

\[ \text{Rate} = k_{obs}[Ni^{2+}][\text{ONH} + \text{ON}] \] (6)

Therefore rate of formation of the complex can be expressed by Eq. (7)

\[ \text{Rate} = d/dt[\text{chelate}] = k_{35}[\text{NiON}] = k_{25}[\text{NiONH}] \] (7)

which can be written as given in Eq. (8)

\[ k_{obs}[Ni^{2+}][\text{ONH} + \text{ON}] = k_{35}[\text{NiON}] + k_{25}[\text{NiONH}] \] (8)
Using steady state approximation for the intermediates (NiON) and (NiONH) and substituting their concentrations in Eq. (8), Eq. (9) is obtained.

\[
\frac{k_{\text{obs}}}{[H^+]^{-1}} = \left[ \frac{k_{3S}(k_{21} + k_{23} + k_{25})k_{43}k_{1}[H^+]^{-1} + k_{23}k_{12}k_{25}}{k_{34} + k_{35} + k_{32}[H^+]} \right] + \frac{1}{(k_{21} + k_{23} + k_{25})} \quad \ldots (9)
\]

The specific rate constants for the pyridine-2-carboxylic acid and amino acids are comparable due to their similar characteristics. In addition, if the ion-pair dissociative mechanism is operative, then \(k_{12}\) and \(k_{43}\) should be comparable with the rate constants for other neutral and uninegative ligands, respectively.

The rate constant for the reaction of neutral ligands with Ni(II) is about \(5 \times 10^3 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\). Similarly, the rate constant for uninegative ligands reacting with Ni(II) is about \(3.4 \times 10^4 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\).

Using these values of \(k_{12}\) and \(k_{43}\) in Eq. (9), the values of \(k_{34}/k_{3S}, k_{2S}/k_{23}\) and \(k_{21}\) were obtained by non-linear least square fit analysis. The values of these rate constants were further modified by the method of successive approximation to give finally, \(k_{12}=(1.12 \pm 1) \times 10^3 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\); \(k_{43}=(2.8 \pm 2) \times 10^4 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\); \(K_1=(9.3 \pm 0.3) \times 10^{-6} \text{mol dm}^{-3}\); \(k_{34}/k_{35}=1.2 \pm 0.3\); \(k_{25}/k_{23}=3.4 \times 10^{-5}\); \(k_{21}<1\); and \(k_{32}[H^+] \approx 1\).

Substituting the above values of rate constants in Eq. (9), overall rate constants \(k_{\text{obs}}\) have been calculated which show excellent agreement with the experimental values (Table 2).

Equation (9) is simplified to Eq. (10) by using the approximation \(k_{23} \gg (k_{21} + k_{25})\).

\[
k_{\text{obs}} \frac{K_1 + [H^+]}{[H^+]^{-1}} = \frac{(k_{12} + k_{43}K_1[H^+]^{-1})k_{35}K_1}{k_{21}[H^+] + K_1(k_{34} + k_{3S})} + \frac{k_{12}k_{25}}{k_{23}} \quad \ldots (10)
\]

where \(K_1 = k_{23}/k_{32}\).

Under the limiting conditions of low \(pH\) \(k_{12} \gg k_{43}K_1[H^+]^{-1}\) and \(k_{21}[H^+] > K_1\) \((k_{34} + k_{3S})\) and taking logarithms on both sides Eq. (11) is obtained

\[
\log k_{\text{obs}} = \log K_1 + [H^+] = pH + \log \frac{k_{43}k_{35}K_1}{k_{34}} \quad \ldots (11)
\]

Equation (11) predicts a linear plot of unit slope and an intercept of \(\log k_{43}k_{35}K_1/k_{34}\) under the limiting conditions of low \(pH\). At high \(pH\), the opposite limiting conditions are taken and we get Eq. (12)

\[
\log k_{\text{obs}} = \log K_1 + [H^+] = pH + \log \frac{k_{43}k_{35}K_1}{k_{34} + k_{3S}} \quad \ldots (12)
\]

Eq. (12) again predicts a linear plot with unit slope and an intercept of \(\log k_{43}k_{35}K_1/(k_{34} + k_{3S})\). This is actually found to be so (see Fig. 1). Equations (11) and (12) obtained from Eq. (10) are exactly the same as obtained from Eq. (2) by Jordan and Voss. This

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Ni}^{2+} \times 10^2 \text{mol dm}^{-3} & \textbf{pH*} & 10^{-3} \times k_{\text{obs}} \text{dm}^3\text{mol}^{-1}\text{s}^{-1} & \text{Expl} & \text{Calc} \\
\hline
5.00 & 2.58 & 0.08 & 0.08 & \\
5.00 & 2.71 & 0.12 & 0.12 & \\
5.00 & 2.83 & 0.15 & 0.15 & \\
5.00 & 3.01 & 0.22 & 0.22 & \\
1.00 & 3.37 & 0.47 & 0.48 & \\
1.00 & 3.58 & 0.72 & 0.73 & \\
1.00 & 3.77 & 1.11 & 1.08 & \\
0.50 & 4.06 & 1.71 & 1.80 & \\
0.50 & 4.12 & 1.97 & 2.00 & \\
0.50 & 4.23 & 2.38 & 2.40 & \\
0.50 & 4.35 & 3.30 & 2.99 & \\
0.50 & 4.41 & 3.50 & 3.31 & \\
0.50 & 4.49 & 3.88 & 3.78 & \\
0.50 & 4.60 & 4.30 & 4.44 & \\
0.50 & 4.63 & 4.80 & 4.68 & \\
0.50 & 3.74 & 5.44 & 5.36 & \\
0.50 & 4.87 & 6.48 & 6.44 & \\
0.50 & 5.02 & 7.68 & 7.66 & \\
0.50 & 5.24 & 8.40 & 9.20 & \\
0.50 & 5.39 & 10.30 & 10.40 & \\
0.50 & 5.96 & 11.80 & 12.40 & \\
0.10 & 6.15 & 13.20 & 13.80 & \\
0.10 & 6.29 & 15.00 & 14.20 & \\
0.10 & 6.37 & 16.40 & 15.80 & \\
\hline
\end{tabular}
\caption{Overall Rate Constants for the Reaction Between \text{Ni}^{2+} \text{and Pyridine-2-carboxylic Acid Calculated Using Modified Scheme 2}}
\end{table}

*Values taken from ref. 1.
conclusion predicts that the ratio $k_{25}/k_{23}$ is very small. This may be because similar expressions (11) and (12) can be obtained from two different equations (10) and (2) only when $k_{25}/k_{23}$ is negligible.

Calculation of step-rate constants

In order to calculate specific rate constants for binding of Ni$^{2+}$ by pyridine-2-carboxylic acid, Eq. (9) is simplified and rearranged to Eq. (13) using the approximations, $k_{35} > (k_{34} + k_{32}[H^+])$ and $k_{23} > (k_{21} + k_{23})$.

$$k_{obs} \frac{K_1 + [H^+]}{[H^+]} = \frac{(k_{12} + k_{43}K_1[H^+]^{-1})(1 + k_{25}/k_{23})}{(k_{34}/k_{35})(k_{12}/k_{43}K_1[H^+]) + (k_{34}/k_{35} + 1)(1 + k_{25}/k_{23})}$$

... (13)

A non-linear least square analysis of the data in Table 2 was used to calculate $k_{12}$, $k_{43}$, $k_{34}/k_{35}$ and $k_{25}/k_{23}$ in Eq. (13). The resulting values are reported in Table 3.

In Table 1, we have compared the values of the intercepts log $k_{43}K_3K_1/K_{34}$ and log $k_{43}K_3K_1/(k_{34} + k_{35})$ at low and high pH, respectively, as obtained from Fig. 1 with the values calculated based on our Scheme 2 and with those of Jordan and Voss$^1$. An excellent agreement between the values calculated using Scheme 2 and experimental values lends sufficient support to our suggested modified reaction scheme.

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References


<table>
<thead>
<tr>
<th>Specific rate constants</th>
<th>Values</th>
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<tbody>
<tr>
<td>$k_{12}$</td>
<td>$4.19 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{43}$</td>
<td>$2.88 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{34}/k_{35}$</td>
<td>1.45</td>
</tr>
<tr>
<td>$k_{25}/k_{23}$</td>
<td>$4.53 \times 10^{-5}$</td>
</tr>
</tbody>
</table>