Kinetics and mechanism of complex formation between (oxalato)pentaamminecobalt(III) and Ni(II) in aqueous medium

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The kinetics of the reversible complexation of oxalatopentaamminecobalt(III) with Ni^{2+} has been investigated at 15-35°C and \( I = 0.30 \text{ mol dm}^{-3} \). At 25°C, \( k_f = (2.98 \pm 0.31) \times 10^3 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}, \Delta H_f = 54.5 \pm 3.7 \text{ kJ mol}^{-1}, \Delta S_f = +3.3 \pm 12.3 \text{ JK}^{-1}\text{mol}^{-1}, \text{ and } k_r = (57.9 \pm 2.2) \text{ s}^{-1}, \Delta H_f = (60.4 \pm 1.5) \text{ kJ mol}^{-1}, \Delta S_f = -8.8 \pm 5.0 \text{ JK}^{-1}\text{mol}^{-1} \), where \( k_f \) and \( k_r \) denote the rate constants for the formation and dissociation of the binuclear species, \((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Ni}^{3+}\) respectively. It is likely that the binuclear species exists in equilibrium between its monodentate and chelated forms, the half bonded oxalate moiety of the cobalt (III) substrate acting as a chelating ligand. The dissociation of Ni^{2+} from the monodentate form of the binuclear species is rate-limiting while the formation of such a species from the reactants is predominantly governed by the rate limiting water dissociation from Ni(OH)$_2$.6$.

The solution equilibrium involving the formation of binuclear species of Ni(II) with \((\text{NH}_3)_5\text{CoC}_2\text{O}_4^+\) has been investigated spectrophotometrically1. Comparison of the stability constant of \((\text{NH}_3)_5\text{CoC}_2\text{O}_4^+\text{Ni}^{3+}\) with those of mono-acetatonickel (II), monooxalatonickel (II) and monooxalatoferric (II) \((\text{EtOCOCO}_2\text{Ni}^+)\) indicated that Ni(II) might be chelated by the oxalate moiety in the binuclear species mentioned above. The observed higher reactivity of the binuclear species2 relative to its proton complex analogue, i.e. \((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^+\) in promoting oxalate substitution by water (auration) at the cobalt (III) centre, was also consistent with the activation of Co(III) bound carboxylate group by Ni(II) as expected for the chelate form of the binuclear species. It is also of interest to note that a comparison of dissociation rate constant of analogous Fe(III) species, viz \((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Fe}^{4+}\) with those of FeOCOCO$_2^+$ and Fe$_2$CCH$_3$Cl$_x$ \((x = 0, 1, 2; y = 3, 2, 1)\) \{\(k_d(\text{Fe}_2\text{CR}^2+)/k_d(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Fe}^{4+}) = 4.0 \) at 25°C\}$^3$ supported the chelate nature of the binuclear species. These results, however, called for further work in order to probe into the nature of the binuclear species through the study of kinetics and mechanism of reversible complexation of Ni(II) by \((\text{NH}_3)_5\text{CoC}_2\text{O}_4^+\). The present work, which is an attempt in the direction, reports on the rate and activation parameters for the formation and dissociation of \((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Ni}^{3+}\) in aqueous medium.

Material and Methods

The complex (oxalato) pentaamminecobalt (III) perchlorate, \([\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}]\text{(ClO}_4)_2\), was prepared by the standard procedure$^4$ and its analytical data (cobalt, \text{NH}_3 and oxalate) were in excellent agreement with those calculated theoretically. The spectral parameter of \((\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{H}^+ [\lambda_{max}, \text{nm} (\varepsilon, \text{dm}^3\text{mol}^{-1}\text{cm}^{-1})]: 507 (74.0)\) in 0.1 mol dm$^{-3}$ HClO$_4$ was in good agreement with the previously reported values$^1$. Aqueous solution of nickel(II) nitrate (BDH) was estimated by complexometric titration using Na$_2$EDTA solution$^6$. Solutions were prepared in doubly distilled water, the second distillation being made from alkaline KMnO$_4$. Ionic strength was adjusted using sodium perchlorate. A Jasco model 7800 recording spectrophotometer was used to record the spectra.

Rate measurements

The kinetics of complexation of the oxalato complex with Ni(II) was investigated at 15.0 \( \leq t \leq 35.0\)°C and \( I = 0.3 \text{ mol dm}^{-3} \). The kinetics were studied spectrophotometrically at 290 nm using a HI-TECH (UK) SF-51 stopped-flow spectrophotometer equipped with an Apple II GS computer. The reservoir syringes, the flow system and the reaction chamber were thermostated to the desired temperature. The other experimental details were the same as mentioned in earlier work$^3$. The observed pseudo-first order rate constants were calculated by a computer program$^7$ which made a least squares fit of absorbance-time data (absorbance decreased with time) to a single exponential curve applicable to first order kinetics.
The reported observed rate constant is an average from at least seven runs and its error quoted is the standard deviation.

Results and Discussion

The observed pseudo-first order rate constants presented in Table 1 satisfy Eq. (1)

\[ k_{obs} = a[Ni^{2+}]_T + b \] ...

at a given acidity. The linear plots of \( k_{obs} \) versus \([Ni^{2+}]_T\) at each \([H^+]_T\), however, converge to a common acid-independent intercept (= b) while the slopes of such plots (= a) decrease with increasing acidity (see Fig. 1). The parameter b is reconciled with dissociation rate constant of the product binuclear complex. The observed inverse acid-dependence of a is thus reconciled with the protonation preequilibrium of \((NH_3)_sCoC_2O_4^+\) which generates reversibly an unreactive or less reactive dipositive acid form of the cobalt (III) substrate. It is worth noting that the acid form of the oxalato complex was totally unreactive to \(Fe(OH_2)^{2+}\). It is not surprising that a similar situation prevails in the case of \(Ni(OH_2)^{2+}\) also. Consistent with the above mentioned facts Scheme 1 is proposed for which \(k_{obs}\) takes the form

\[ k_{obs} = k_f(K_{d}/([H^+] + K_d))[Ni^{2+}]_T + k_r \] ...

where

\[ k_f = K_{OS}k_{11}k_{22}/(k_{-11} + k_{22}) \] ...

and

\[ k_r = k_{-11}k_{-22}/(k_{-11} + k_{22}) \] ...

Table 1—Rate data for complexation of Ni(II) with \((NH_3)_sCoC_2O_4^{2+}\)

<table>
<thead>
<tr>
<th>([Ni(III)]_T) (mol dm(^{-3}))</th>
<th>(k_{obs}) (s(^{-1}))</th>
<th>(k_{obs}) (s(^{-1}))</th>
<th>(k_{obs}) (s(^{-1}))</th>
<th>(k_{obs}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>15.0±0.1</td>
<td>30.2±1.3</td>
<td>76.8±1.4</td>
<td>108.4±3.0</td>
</tr>
<tr>
<td>10.0</td>
<td>37.8±1.3</td>
<td>93.6±3.0</td>
<td>129.8±4.7</td>
<td>157.0±2.9</td>
</tr>
<tr>
<td>15.0</td>
<td>43.1±1.2</td>
<td>108.5±1.4</td>
<td>151.0±4.1</td>
<td>178.6±4.6</td>
</tr>
<tr>
<td>20.0</td>
<td>51.4±1.3</td>
<td>126.4±2.2</td>
<td>170.5±2.8</td>
<td>206.0±6.6</td>
</tr>
<tr>
<td>30.0</td>
<td>63.8±2.0</td>
<td>159.8±4.2</td>
<td>209.8±5.8</td>
<td>340.8±6.8</td>
</tr>
<tr>
<td>40.0</td>
<td>67.1±1.3</td>
<td>162.4±3.3</td>
<td>243.9±9.0</td>
<td>338.2±4.9</td>
</tr>
</tbody>
</table>

(a) I=0.3, \([Co(III)]_T=2.0-3.0 \times 10^{-4}\) mol dm\(^{-3}\), \(\lambda=290\) nm.
(b) \([H^+]_T=0.010\) for the values in parentheses and \(0.0050\) mol dm\(^{-3}\) for all others.

Fig. 1—Plots of \(k_{obs}\) versus \([Ni^{2+}]_T\) at a and b at 35°C; c and d at 25°C; a and c at \([H^+]_T=0.0050\) mol dm\(^{-3}\); b and d at \([H^+]_T=0.010\) mol dm\(^{-3}\)

\[ RC_2O_4^+ + Ni(OH_2)_6^{2+} \rightleftharpoons R(C_2O_4)Ni(OH_2)_6^{3+} \]

\[ k_{II} \rightleftharpoons k_{-II} \]

\[ RC_2O_4OH^{2+} \rightleftharpoons R(C_2O_4)Ni(OH_2)_5^{3+} (\text{mono}) \]

\[ RC_2O_4Ni(OH_2)_4^{3+} (\text{chel}) \]
Table 2—Rate and activation parameters for formation and dissociation processes

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>15.0±0.1</th>
<th>25.0±0.1</th>
<th>30.0±0.1</th>
<th>35.0±0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1^e$ (s$^{-1}$)</td>
<td>23.8±0.2</td>
<td>57.9±2.2</td>
<td>89.6±1.0</td>
<td>122.5±2.5</td>
</tr>
<tr>
<td>$10^{-3} k_r$ (dm$^3$mol$^{-1}$s$^{-1}$)</td>
<td>1.23±0.13</td>
<td>2.98±0.31</td>
<td>3.99±0.12</td>
<td>6.42±0.05</td>
</tr>
</tbody>
</table>
| $\Delta H^\ddagger$ (kJ mol$^{-1}$) | 60.4±1.5$^b$ | $\Delta S^\ddagger$ (JK$^{-1}$ mol$^{-1}$) | $-8.8±5.0^b$ | \hline
| (54.5±3.7)$^c$ | ( + 3.3±12.3)$^c$ |

(a) Values are average of the values of intercepts of $k_{obs}$ versus $[Ni(II)]_T$ plots at $[H^+]_T = 0.010$ and 0.0050 mol dm$^{-3}$.  
(b) For $k_r$ path  
(c) For $k_f$ path.

In Eq. 3, $K_{OS}$ is the outer sphere association constant. The expressions for $k_f$ and $k_r$ are based on the steady state approximation for the monodentate binuclear species ($NH_3)_2 CO_2CCO_2[Ni(OH_2)]^2^+$ the concentration of which is much smaller than that of the corresponding chelate species. Although the Scheme 1 delineates multistep reactions, the absorbance-time data for every run conforms to a single exponential curve which discounts the possibility of consecutive reactions due to build-up of this monodentate intermediate species. Rate data were analysed by Eq. (2) using values of $k_d$ reported in our earlier work$^b$ and the values of $k_f$ and $k_r$ were determined from the slopes and intercepts, respectively, of $k_{obs}$ versus $[Ni^{2+}]_T$ plots and the corresponding activation parameters are presented in Table 2.

The value of $k_f$ at 25°C is smaller than the water exchange rate constant of Ni(H$_2$O)$_6^{2+}$ but within a factor of 10 ($k_{ex} = 2.7-3.6 \times 10^4$ s$^{-1}$ at 25°C)$^b$. Also, similar rate difference exists in the values of $k_f$ (dm$^3$mol$^{-1}$s$^{-1}$) (25°C, $I = 0$) for monoaion ligands, acetate (15 $\times$ 10$^4$), lactate (2.5 $\times$ 10$^4$) and glycolate (3 $\times$ 10$^4$)$^{10}$. This rate difference is attributed at least partly to a lower value of the outer sphere association constant, $K_{OS}$, for the substrate under consideration. The values of $K_{OS}$ cannot be greater than unity considering the electrostatic effect$^{11}$. It is thus evident that the rate process associated with formation of the binuclear complex is governed predominantly by the rate of water dissociation from Ni(OH$_2$)$_6^{2+}$. Assuming this interpretation, Eq. (3) leads to

$$k_f = K_{OS} k_{11} \quad \text{(i.e. } k_{22} \gg k_{-11}) \quad \ldots \quad (5)$$

Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the formation reaction (see Table 2) also agree with the corresponding activation parameters for the water exchange reaction of Ni(OH$_2$)$_6^{2+}$ ($\Delta H^\ddagger = 45$ to 51 kJ mol$^{-1}$, $\Delta S^\ddagger = + 2.5$ to $+ 15$ JK$^{-1}$ mol$^{-1}$)$^b$. The values of the overall dissociation rate constant for the binuclear complex ($k_f = 58 \pm 2$ s$^{-1}$ at 25°C, see Table 2) is 15 times greater than that of monooxalato Ni(II) ($k_f = 3.6$ s$^{-1}$ at 25°C, $I = 0.3$ moldm$^{-3}$)$^{12}$, but smaller than those for monoglycinatonickel (II) [$k_f = (2.0-2.6) \times 10^2$ s$^{-1}$ at 25°C, $I = 0$] and monolactatonickel (II) [$k_f = (1.7-9.0) \times 10^2$ s$^{-1}$ at 25°C, $I = 0$]$^{10}$ species by a small magnitude only. These rate differences for ligands of comparable basicities can be easily understood in terms of the electrostatic effects considering the charges of the ligands departing from the Ni(II) centre. If it is assumed that $k_{22} \gg k_{-11}$, then $k_f$ takes the form: $k_f = k_{-11} Q$ (see Eq. 4) where $Q = k_{-22}/k_{22}$, i.e., the equilibrium constant for monodentate and chelate forms of the binuclear complex. It is interesting to note that $k_f$ of the monodentate form of the binuclear species (i.e. $k_{11}$ path) is rate-limiting. A lower value of $k_f$ for the binuclear complex relative to that for the monooxalatonickel (II) complex must be due to a relatively lower value of $Q$ for the former. A tentative value of $Q$ ($= k_f/k_{-11}$) for the equilibrium between chelate and monodentate species (see Scheme 1) can be obtained, assuming a value of $k_{-11}$. The reported$^9$ value of $k_{-11}$ of CH$_3$CO$_2$Ni(OH$_2$)$_5^+$ at 25°C ($I = 0$) is 5000 s$^{-1}$. For the Ni(OH$_2$)$_2$CNS$^+$ species the value of $k_{-11}$ calculated from the reported value of its overall formation equilibrium constant ($K = 17$ dm$^3$ mol$^{-1}$ at 25°C, $I = 0.5$ mol dm$^{-3}$)$^{13}$ and its formation rate constant ($k_f = 5 \times 10^3$ mol$^{-1}$ s$^{-1}$ at 25°C, $I = 0.5$ mol dm$^{-3}$)$^{14}$ is 3 $\times$ 10$^2$ s$^{-1}$ at 25°C. Hence using these values as reasonable approximations for $k_{-11}$ for (NH$_3)_2$CoC$_2$O$_4$Ni(OH$_2$)$_5^+$, we obtain $Q = 0.012$ or 0.19 as the lower and upper limits at 25°C. The activation parameters for the dissociation reaction based on the temperature-dependence of $k_f$ are comparable to those for the forward ($k_f$) and the reverse processes ($k_r$) must be alike.

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