Kinetics and mechanism of complex formation between Co(II) and (3-nitrosalicylato)(tetren)cobalt(III) ion in aqueous medium

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Received 29 October 1992; revised 24 May 1993; accepted 7 December 1993

The kinetics of reversible complexation of Co(II) with (3-nitrosalicylato)(tetren)cobalt(III) ion has been investigated by the stopped flow technique at 15-35°C, pH = 5.80-6.90 and I = 0.30 mol dm⁻³ (ClO₄⁻). The formation of the binuclear species, (tetren)CoO₂CC₆H₃(3NO₂)OCO³⁻, occurs via the reaction of Co(OH₂)₆⁺⁺ with the phenoxide form of the cobalt(III) substrate. At 25°C, kₐ = (8.29 ± 0.07) × 10⁴ dm³ mol⁻¹ s⁻¹, ΔH° = 30.6 ± 1.9 kJ mol⁻¹, ΔS° = -48 ± 6 JK⁻¹ mol⁻¹, and kₐ = (35.9 ± 0.4) s⁻¹, ΔH° = 52.7 ± 1.9 kJ mol⁻¹, ΔS° = -39 ± 6 JK⁻¹ mol⁻¹, where kₐ and kₐ denote the rate constants for the formation and dissociation of the binuclear species, (tetren)CoO₂CC₆H₃(3NO₂)OCO³⁻, respectively. Data are consistent with a mechanism. The first bond formation between Co(OH₂)₆⁺⁺ and the coordinated salicylate of the cobalt(III) substrate in the encounter complex is rate limiting. The binuclear species exists in dynamic equilibrium between its monodentate and chelate form.

Recent studies have demonstrated that the substituted salicylatopentaminecobalt(III) substrates act as potential chelating agents towards Al(III), Fe(III), Ga(III), and Ni(II) despite the unfavourable electrostatic repulsion between the like charge centres in the binuclear species. These results prompted us to extend our work to relatively more labile metal ion, Co(OH₂)₆⁺⁺. The present work reports the kinetics and mechanism of binuclear complexation between Co(OH₂)₆⁺⁺ and (3-nitrosalicylato)(tetren)cobalt(III) ion.

Experimental

The (3-nitrosalicylato)(tetren)cobalt(III) perchlorate was received as a mixture of αβR and αβS isomers. The stock solution of cobalt(III) perchlorate was standardised by complexometric titration using Na₂EDTA. Lutidine buffer was used to adjust pH. Analar grade reagents were used. Solutions were prepared in deionised doubly distilled water. The ionic strength adjustments were made using NaClO₄.

The pH measurements were made with an Elanco digital pH meter, model LI 120, equipped with a combination electrode glass-Ag/AgCl, NaCl (2 mol dm⁻³) (Model CL 51). Standard NBS buffers (pH = 4.01, 6.86, and 9.20) were used for the calibration of the pH meter. The concentrations of H⁺ (= aH⁺ / fH⁺) were calculated from the pH data using the calculated values of the activity coefficient of H⁺ at 15°, 25°, 30° and 35°C (fH⁺ = 0.3 mol dm⁻³) respectively. All UV-visible spectra were recorded on a Jasco model 7800 spectrophotometer with 1 cm matched quartz cells. Analysis of rate data was made by a nonlinear least squares computer program adapted to Wipro Land Mark 4860 computer. Kinetic measurements were made with a fully automated HI-TECH (U.K.) SF-51 stopped-flow spectrophotometer. The drive syringes and cell compartments were thermostated at the desired temperature with an accuracy of ±0.1°C.

Rate measurements

The kinetics of complexion of the title complex with Co(II) was investigated at 15.0 ≤ temp., °C ≤ 35.0, [Co₂⁺]ₜ = (2-20) × 10⁻³ mol dm⁻³ and I = 0.3 mol dm⁻³ (NaClO₄) with [complex]ₜ = (2-9) × 10⁻⁵ mol dm⁻³ and pH = 5.80-6.90 (see Table I). The reaction was monitored at 340 nm. The other experimental details were the same as reported earlier.

All runs were made under pseudo-first order conditions and the rate constants were calculated by an Apple IIGS PC using ADS2 software suite available from M/s HI-Tech Scientific Ltd (U.K.) which made a least squares fit of absorbance-time data (absorbance increased with time) to a single exponential curve as applicable to first order kinetics. Each rate constant reported is average of at least seven replicate measurements for a given run and its error quoted as a standard deviation.

Results and discussion

Dissociation constant (pKₐOH):

The absorbance of the (3-nitrosalicylato-
1.0

Fig. 1—Spectra of \((\text{tetren})\text{CoO}_2\text{CC}_6\text{H}_3(3\text{NO}_2)\text{OH}^{2+}\) in the presence and absence of \(\text{Co(II)}\) at \(pH = 6.85\) and \(30°C\): (1)-\(\text{Co(II)}\) (0.0075 mol dm\(^{-3}\)), (2)-\(\text{Co(III)}\) substrate only (7.5 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\)), and (3)-\(\text{Co(III)}\) substrate (7.5 \(\times\) 10\(^{-5}\) mol dm\(^{-3}\)) + \(\text{Co(II)}\) (0.0075 mol dm\(^{-3}\)).

to \((\text{tetren})\text{cobalt(III)}\) perchlorate at 400 nm increased with increase in \(pH\) which is attributed to the formation of the highly absorbing phenoxide form of the complex. The dissociation constant \(K_m\) of the uncoordinated phenol group was determined using the absorbance data at 400 nm for \([\text{complex}]_f = 1.6 \times 10^{-4}\) mol dm\(^{-3}\) in the \(pH\) range 7.0-8.20 (Tris-buffer) \((I = 0.3\) mol dm\(^{-3}\)) using the linearized form of Eq. (2) \(\left(\varepsilon_{\text{obs}} - \varepsilon_1\right)^{-1} \text{versus } [H^+]^{-1}\) plot

\[
\varepsilon_{\text{obs}} = \left(\varepsilon_1 + \varepsilon_2 K_{\text{OH}}/[H^+]\right)/(1 + K_{\text{OH}}/[H^+]) \quad \ldots (2)
\]

where \(\varepsilon_{\text{obs}}, \varepsilon_1, \varepsilon_2\) denote the observed molar extinction coefficient of the complex at a given \(pH\), and that of the phenol and phenoxide form respectively. \(\varepsilon_1 = \varepsilon_{\text{obs}}\) at \([H^+] = 0.10\) mol dm\(^{-3}\) was used to fit the data. We obtained the values of \(pK_{\text{OH}} = 7.61 \pm 0.03, 7.56 \pm 0.03, \) and \(7.50 \pm 0.03\) at \(25.0, 30.0\) and \(35.0°C\) respectively.

\section*{Equilibrium constant \((K_M)\)}

The equilibrium constant, \(K_M\), for the reaction shown in Eq. (3) was calculated at \(25°C\) \((I = 0.3\) mol dm\(^{-3}\)) from the absorbance data at 387 nm of the solutions containing a fixed \([\text{complex}]_f\) and varying amount of \([\text{Co}^{2+}]_f = 0.002-0.015\) mol dm\(^{-3}\) at a fixed \(pH\) \((=6.40 \pm 0.02)\) after making due allowance for the absorbance of \([\text{Co}^{2+}]_f\).

\[
(\text{tetren})\text{CoO}_2\text{CC}_6\text{H}_3(3\text{NO}_2)\text{O}^+ + \text{Co}^{2+} \rightleftharpoons (\text{tetren})\text{CoO}_2\text{CC}_6\text{H}_3(3\text{NO}_2)\text{OCO}_3^+ \quad \ldots (3)
\]

The value of equilibrium constant, \(K_M\), was calculated from the linearized form of Eq. (4)

\[
\varepsilon'_{\text{obs}} = \varepsilon_1 + \varepsilon_2 K_{\text{OH}}/[H^+] + \varepsilon_3 K_{\text{OH}}K_M[\text{Co}^{2+}]_f/[H^+] \\
1 + K_{\text{OH}}K_M[\text{Co}^{2+}]_f/[H^+] \quad \ldots (4)
\]

where \(\varepsilon'_{\text{obs}} = (A_{\text{obs}} - A_{\text{Co}})/[\text{complex}]_f\), \((A_{\text{obs}} - A_{\text{Co}})\) is the observed absorbance of the reaction mixture corrected for the absorbance of \(\text{Co(II)}\) \((A_{\text{Co}})\), \(\varepsilon_3\) is the molar extinction coefficient of the binuclear species and all other terms have usual meaning. The value of \(K_M\) was found to be \(1039 \pm 175\) dm\(^3\) mol\(^{-1}\). The stability constant of the binuclear species relative to that of \(\text{Co(II)}\)-3\text{NO}_2\text{salicylate} \((\log K_{\text{ML}} = 5.76 \pm 0.04\) at \(I = 0.0035\) mol dm\(^{-3}\), \(25°C\)) reflect the strong destabilising effect of the electrostatic repulsion between the like charge centres in the former species.

\section*{Kinetics of complexation}

Formation of the binuclear complex is indicated from the spectra of the complex in the presence and absence of \([\text{Co}^{2+}]\) (see Fig. 1). No spectral evidence of complex formation between \(\omega\)-\text{nitrophenol} and \(\text{Co}^{2+}\) under comparable conditions \([\text{[\omega-nitrophenol]} = 1.0 \times 10^{-4}\) mol dm\(^{-3}\), \([\text{Co}^{2+}] = 1.0 \times 10^{-2}\) mol dm\(^{-3}\), \(pH = 6.90\) at \(30°C\)] was observed.
The observed pseudo-first order rate constants at varying pH and $[\text{Co}^{2+}]_T$ are collected in Table 1. The plots of $k_{\text{obs}}$ versus $[\text{Co}^{2+}]_T$ at different pH's are linear and converge to a common acid-independent intercept, while gradients of such plots increase with increase in pH (Fig. 2) in the pH range 5.80-6.90. The acid independent intercept is reconciled with the dissociation rate constant of the binuclear species, which is not sensitive towards H$^+$ and OH$^-$ in the pH range studied or the acid or base components of the buffers used. Consistent with these facts and assuming that the chelated species is formed via the mono-bonded intermediate the possible reaction pathways are delineated in Scheme 1 for which $k_{\text{obs}}$ takes the form

$$k_{\text{obs}} = k_i (K_{\text{OH}} / ([\text{H}^+] + K_{\text{OH}})) [\text{Co}^{2+}] + k_r$$ (5)

where the overall formation rate constant ($k_i$) and dissociation rate constant ($k_r$) of the binuclear species (tetren)$\text{CoO}_2\text{CC}_6\text{H}_3(3\text{NO}_2)\text{OCO}^{3+}$, are given by Eqs (6) and (7) respectively

$$k_i = K_{\text{on}} k_{11} k_{22} / k_{22} + k_{-11}$$ (6)

$$k_r = k_{-11} k_{22} / k_{22} + k_{-11}$$ (7)

In Eq. (6) $K_{\text{on}}$ is outer sphere association constant of $\text{Co(OH}_2)_{26}^{3+}$ with the phenoxide form of the complex, and $k_{11}$ and $k_{-11}$ denote the rate con-
stant for the individual steps [Eqs (6) and (7)]. Values of \( k_i \) and \( k_{-i} \) were calculated by fitting the rate data to Eq. (5) by a weighted least squares program which minimized the residuals, \( \sum w_i(k_{\text{calc}}-k_{\text{obs}})^2 \) where \( w_i = \frac{1}{\sigma(k_{\text{obs}})^2} \). The corresponding activation parameters are presented in Table 2. The values of \( k_{\text{obs}} \) and \( k_i \) reproduce the rate constants satisfactorily supporting the validity of the proposed reaction scheme.

It is worth noting that there is no evidence for the reaction of \( \text{Co(OH}_2\text{)}^{2+} \) with dipositive phenol form of the cobalt(III) substrate. Similar observation was also made in the reaction of \( \text{Ni(OH}_2\text{)}^{2+} \) with (substituted salicylato)pentaminecobalt(III) substrates. \( \text{N}_2\text{Co}_2\text{CC}_6\text{H}_4(X)\text{OH}_2^+ \), where the pentamine residues are SNH\(_3\), (en\(_2\))(NH\(_3\)) (cis-isomer), tetaethylenepentamine for X = 3NO\(_2\) and 5NH\(_3\) for X = 5NO\(_2\) (ref. 5). The value of \( K_{\text{M}} \) calculated from the kinetic data at 25°C (\( K_{\text{M}} = k_i/k_{-i} = 2309 \pm 32 \text{ dm}^3 \text{ mol}^{-1} \)) is comparable with the same obtained from the equilibrium measurements. The formation rate constant \( k_i = K_{\text{os}}k_{11} \) when \( k_{22} > k_{-11} \) [see Eq. (6)]. The value of the interchange rate constant, \( k_{11} \), can be predicted if value of \( K_{\text{os}} \) is known. Based on the diffusion limited ion-pairing and purely coulombic concepts, the values of \( K_{\text{os}} \) are 1.4, 0.3 and 0.07 dm\(^3\) mol\(^{-1}\) for \(+2, -1\); \(+2, 0\); and \(+2, +1\) ion-pairing processes at 25°C respectively\(^8\). Using the value of \( K_{\text{os}} = 0.07 \text{ dm}^3 \text{ mol}^{-1} \), \( k_{11} = k_i/K_{\text{os}} \) turned out to be \( 1.2 \times 10^6 \text{ s}^{-1} \) at 25°C, which compare satisfactorily with the water exchange rate constant of \( \text{Co(OH}_2\text{)}^{2+} \) (\( k_{\text{os}} = (1.1-2.4) \times 10^6 \text{ s}^{-1} \) at 25°C)_\(^9\). Hence the first bond formation between the ligand and the Co(II) centre within the encounter complex involves essentially dissociative interchange \((I_0)_{10}\). Values of \( \Delta H^* \) and \( \Delta S^* \) for the formation reaction differed from those reported for the water exchange reaction of \( \text{Co(OH}_2\text{)}^{2+} \)

\[
\Delta H^* = (33.4-43.5) \text{ kJ mol}^{-1}, \quad \Delta S^* = (-17 + 21) \text{ JK}^{-1} \text{ mol}^{-1},
\]

This difference might arise from the differential solvation effects of the initial state of the highly charged encounter complex and the corresponding transition state.

The value of the dissociation rate constant, \( k_{-i} \), is at least 64 times greater than that of \( \text{Ni(OH}_2\text{)}^{2+} \) and \( \text{Co(OH}_2\text{)}^{2+} \) complexes reported in the literature\(^1\). Based on the assumption \( k_{22} > k_{-11}, \) takes the form \( k_i = k_{-11}Q \) [see Eq. (7)] where \( Q = k_{22}/k_{22} \) (Q is the equilibrium constant for monodentate and chelated forms of the binuclear complex). Using a rough estimate of \( k_{-11} \) (equal to that of imidazole-Co(II) system)\(^12\) as 507 s\(^{-1}\), the value of \( Q = (k_i/k_{11}) \) was found to be 0.11 at 25°C. However, the value of dissociation rate constant \( k_{-11} \) for Co(II)-carboxylate (O-bonded) monodentate ligand may be higher than that of Co(II)-imidazole (N-bonded). In that case a much lower value of Q is expected. This evidently suggests that the binuclear species exists in equilibrium, monobonded = chelated form, with the equilibrium driven favourably towards the chelate form.

**Acknowledgement**

ANA is thankful to Prof. A C Dash, Department of Chemistry, Utkal University, for providing all facilities and valuable suggestions for this work.

**References**


