Kinetics and mechanism of anation of hydroxopentaaquarhodium(III) ion by DL-methionine

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The kinetics of anation of \([\text{Rh(OH}_2)_6\text{(OH)}_2]^{2+}\) by DL-methionine has been studied spectrophotometrically by monitoring the characteristic absorption peak of the product complex \((\lambda_{\text{max}} = 262 \text{ nm})\) as a function of substrate and ligand concentrations in the 50-65°C temperature range and in the pH range 2.5-4.3. The rate law involving the outer sphere complex formation has been established at pH 4.3 as

\[
d\left[\text{Rh(OH}_2)_6\text{(OH)}_2\right]^{2+}\text{[LH]}\over dt = k_1K_1[\text{Rh(OH}_2)_6\text{(OH)}_2]^{2+}\text{[LH]}\left(1 + K_F\text{[LH]}\right)
\]

The activation parameters have been calculated and compared with those for water exchange reaction and other substitution reactions. A mechanism involving the prior formation of an outer sphere complex followed by associative interchange \((I_1)\) is suggested where both bond making and bond breaking are equally important in the transition state.

Among the platinum metals rhodium is unique due to its wide applications, and the diverse types of mechanisms it exhibits for ligand substitution reactions. For some ligands the anation rates are slow and a dissociative mechanism was proposed; by contrast an associative mechanism and a concerted mechanism was proposed for the anation of \([\text{Rh(OH}_2)_6\text{Cl}]^{+}\) and \([\text{Rh(OH}_2)_5\text{Cl}^{2+}\) by the different entering ligands. In view of the diverging mechanisms proposed so far for the anation studies on aqua rhodium(III) complexes we have planned to study the mechanistic aspects of the aqua ligand substitution from \([\text{Rh(OH}_2)_6\text{Cl}]^{+}\) and \([\text{Rh(OH}_2)_5\text{Cl}^{2+}\) by some selected ligands.

This note presents the kinetic behaviour of DL-methionine (in zwitterionic form) as an anating ligand towards hydroxopentaaquarhodium(III) cation.

**Experimental**

The complex \([\text{Rh(OH}_2)_6\text{Cl}_4]^{3-}\) was prepared according to the method of Ayres and Forrester, characterised spectrally \((\lambda_{\text{max}} = 396 \text{ nm}, \epsilon = 62, 311 \text{ nm}, \epsilon = 67.4)\) and by elemental analysis. The experimental condition was maintained to obtain the substrate complex \([\text{Rh(OH}_2)_6\text{(OH)}_2]^{2+}\) (complex-I) by adjusting the pH of the solution to 4.3 where ~90% of the perchlorate salt was obtained as the hydroxopentaaqua species. Above this pH (~4.5) the solution becomes turbid, probably due to the precipitation of insoluble hydroxides and thus at further higher pH the study was restricted. The ligand DL-methionine (LH) functions as a tridentate \((S,N,O)\) donor. The product of the reaction between complex-I and DL-methionine was prepared by mixing these in different molar ratios, viz., 1:1, 1:2, 1:3, 1:4 and 1:10 thermostated at 60°C for 48 hours. The absorbance spectra exhibited the same nature having \(\lambda_{\text{max}}\) at 262 nm with almost same absorbance. The spectral difference between the substrate and the product complex has been shown in Fig. 1. The large spectral shift to lower wavelength of the product in comparison to substrate and other complexes indicates the sulphur coordination of the ligand. It was not possible to isolate the product complex, but the composition of the product in solution was determined by Job's method of continuous variation. The metal-ligand ratio was found to be 1:1. The pH of the solution was adjusted by adding NaOH/HClO_4 and the measurements were carried out with the help of a Systronics digital pH meter with an accuracy of ±0.01 unit. The temperature of the reaction bath was adjusted within ±0.1°C. Doubly distilled water was used to prepare all the kinetic solutions. All other chemicals used were either A.R. grade or purified before use. The reactions were carried out at constant ionic strength (0.1 mol dm\(^{-3}\) NaClO_4).

**Kinetic run**

The kinetics of the anation of \([\text{Rh(OH}_2)_6\text{(OH)}_2]^{2+}\) by DL-methionine was studied by following the development of the absorbance peak at 262 nm using a Shimadzu UV-190 spectrophotometer. Conventional mixing technique was followed and pseudo-first order condition was employed for all the reactions. The rate constants \((k_{\text{obs}})\) were obtained from the plots of \(\ln(A_o - A_i)/(A_o - A)\) against time, where \(A_o, A, A_i\) and \(A_{\infty}\) are the absorbances at the outset, at time \(t\) and at infinite time (or after the completion of
the reaction) respectively. The reported rate data (represented as an average of duplicate runs) are reproducible within ±4%.

Results and discussion

At a fixed excess concentration of DL-methionine, pH, ionic strength and temperature, the rate of the reaction was found to be first order in [complex-I] i.e.,

\[
\frac{d[\text{complex-II}]}{dt} = k_{\text{obs}}[\text{complex-I}] \quad \ldots (1)
\]

under the conditions [complex-I] = 2.5 × 10⁻⁴ mol dm⁻³, [ligand] = 5.0 × 10⁻³ mol dm⁻³, temp. = 60°C and µ = 0.1 mol dm⁻³ (NaClO₄). The rate increased from 0.22 to 5.52 s⁻¹ when pH was changed from 2 to 4.3.

The enhancement of \(k_{\text{obs}}\) values with increase in pH can be explained by considering equilibria (2)-(4).

\[
[Rh(OH)_2]^{3+} + K_{\text{eq}} [Rh(OH)_2]_5(OH)_2^2+ + H^+ \quad \ldots (2)
\]

\[
\text{CH}_3\text{S.CH}_2\text{CH}_2\text{C} - \text{COOH} \quad K_1
\]

\[
\text{LH}^+ \quad \text{NH}_3^+ \\
\]

\[
\text{CH}_3\text{S.CH}_2\text{CH}_2\text{C} - \text{COO}^- + H^+ \quad \ldots (3)
\]

The \(pK_a\) value of equilibrium (2) is 3.3, an average value of two reported values at 25°C. With increase in pH the ratio of hydroxopentaaqua to hexaaqua species increases. Hydroxoqua complex due to the π-bonding ability of –OH group facilitates the replacement of aqua molecule in the reaction and is more reactive than the hexaaqua species; hence with the increase in pH the reaction becomes faster. On the other hand the ligand methionine can exist in three different forms. The \(pK_1\) and \(pK_2\) values are 2.24 and 9.07 at 25°C. Thus we see that with increase in pH in the lower pH range the percentage of the deprotonated form increases and then the zwitterionic form (LH) predominates which also partly accounts for the enhancement of rate with increase in pH.

The concentration of zwitterionic methionine was varied in the range 2.5 × 10⁻³ to 10.0 × 10⁻³ mol dm⁻³ at fixed [complex I] (2.5 × 10⁻⁴ mol dm⁻³), pH (4.3), ionic strength (0.1 mol dm⁻³ NaClO₄). The rate increases with the increase in [ligand] at 50, 55, 60 and 65°C and tends to approach a limiting value at higher ligand concentration (Fig. 2). This happens to be due to the completion of outersphere association at higher concentration of the ligand. Naturally any further change in the ligand concentration is unable to change the immediate environment of the complex ion. Since the complex ion reacts with its immediate vicinity, further change in concentration of the ligand will not affect the reaction rate. That is why the gradual approach towards the limiting rate is observed.

Scheme 1 can be proposed to explain the variation of rate due to change in concentration of the incoming ligand.

\[
\text{LH} + [\text{Rh(OH)}_2]_5(\text{OH})_2^2+ \xrightarrow{K_{\text{eq}}} [\text{Rh(OH)}_2]_5(\text{OH})_2^2+ + \text{LH} \\
\text{Fast} \\
\text{Complex-I} \\
\text{Outersphere association}
\]

\[
[\text{Rh(OH)}_2]_5(\text{OH})_2^2+ + \text{LH} \xrightarrow{k_{\text{slow}}} [\text{Rh(OH)}_2]_5(\text{OH})(\text{L})_2^2+ + \text{H}_2\text{O}
\]

[\text{Rh(OH)}_2]_5(\text{OH})(\text{L})_2^2+ \xrightarrow{K_{\text{eq}}} \text{LH} \xrightarrow{K_{\text{eq}}} \text{[Rh(OH)}_2]_5(\text{OH})(\text{L})_2^2+
\]

\[
\text{Fast} \\
\text{Chelation} \\
\text{Complex-II}
\]

\[
\text{Scheme 1}
\]
 Along with this the large negative entropy of activation suggests significant ligand participation in the transition state.

From the experimental evidences we can suggest that anation of \([\text{Rh(OH}_2)_5\text{(OH)}]^2^+\) by \(\text{dl-methione}\) proceeds through an associative interchange mechanism. The complex cation and the entering ligand form an outersphere association which is stabilised through H-bonding. The equilibrium process is very rapid. The slow step is the interchange step in which ligand enters in the innersphere from the outersphere. In this transition state, both bond formation and the bond rupture are equally important. The lower \(\Delta H^*\) in comparison to the aqua exchange process and the significantly negative value of entropy of activation supports the above proposition. The positive enthalpy change due to rupture of Rh(III)-OH bond is partially compensated by the negative enthalpy change due to the new bond formation between Rh(III)-methionine. Moreover, in the associated...
ative activation, the entering ligand and the departing ligand both are attached to the central metal atom, i.e., a compact transition state is obtained in comparison to the initial reactants. As a result the degrees of freedom of the molecules in the activated state are reduced and we observe a drop in the entropy value.

References
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