Kinetic & Mechanistic Studies on Substitution Reaction of Aquo-ligands from cis-Diaquo-bis(biguanide)cobalt(III)/chromium(III) Ions in Aqueous Medium

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The kinetics of substitution of aquo ligands from cis-diaquo-bis-(biguanide)chromium(III)/cobalt(III) ions by L-histidine in aqueous medium have been studied spectrophotometrically. The following rate law has been established in pH range of 3.85 to 5.57:

$$\frac{d[\text{Complex-II}]}{dt} = k [\text{Complex-I}]_{\text{total}} [\text{Ligand}]$$

where, Complex-II = \([\text{M(BigH)}_2(\text{Hist})F]^{2+}\); Complex-I = \([\text{M(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) and ligand = L-histidine; M = Co(III), Cr(III).

In this equation \(K_e\) is the ion-pair equilibrium constant and \(k_e\) the rate constant for interchange of outer-sphere complex to inner-sphere complex. The reaction rates are found to be pH dependent in the pH range of 3.85 to 5.57. Values of activation parameters, \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) have been evaluated. The results are consistent with a mechanism involving outer-sphere association of reactants followed by associative interchange of this outer-sphere complex into the product.

The earlier works\(^1\) on ligand substitution reactions in octahedral complexes indicate that the reactions of Co(III) and Cr(III) systems proceed through I\(a\) and I\(d\) path respectively. However, exceptions\(^6\) -\(^{11}\) are not rare and experimental evidences have been adduced which point out that depending on the nature of the system, I\(a\) or I\(d\) mechanism may operate both for Co(III) and Cr(III). Banerjea and coworkers\(^8\) studied base hydrolyses of \([\text{M(NH}_3\text{MNCS)}_2^+\) [M = Co(III), Cr(III)] and Rh(III)] in aquo-organic mixed solvents and observed a significant difference in relative degree of M-NCS bond cleavage [significantly higher for Cr(III)] and M-OH bond making considerably more pronounced for Co(III) and Rh(III) in the three different cases studied. Chatterjee and co-workers\(^10\) studied base hydrolysis of \([\text{Cr(NH}_3\text{)}_5\text{N}_3\text{F}^+]\) and suggested dissociative mechanism whereas Banerjea and coworkers\(^11\) studied base hydrolysis of \([\text{Co(NH}_3\text{)}_5(S_2\text{O}_3)^2^+\) and suggested associative character of the reaction. It was therefore thought worthwhile to study the anation reactions of similar aquo complexes of Co(III) and Cr(III), and therefore selected systems like \([\text{Co(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) [where M = Co(III), Cr(III)] and incoming ligands, such as pyridine carboxylic acids and a series of amino acids for anation reactions.

The present paper relates to the reaction:

\[\text{cis}[\text{Co(BigH)}_2(\text{H}_2\text{O})_2]^{2+} + \text{Hist.H}^+ \rightarrow [\text{Co(BigH)}_2(\text{Hist.H})]^{3+} + \text{H}_2\text{O} + \text{H}_3\text{O}^+\]

where M = Co(III), Cr(III).

Materials and Methods

\(\text{cis}[\text{Co(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) (Complex-I) was prepared as follows: hydroxoaquobis(biguanide)cobalt(III) sulphate was prepared by the method of Ray and Ghose\(^15\). The perchlorate salt was prepared \textit{in situ} by metathesis of the complex sulphate with barium perchlorate in solution. \(\text{cis}[\text{Cr(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) (Complex-I) was prepared \textit{in situ} by the methods described in literatures\(^13\) -\(^{15}\). Absorption spectra of 0.005 mol dm\(^{-3}\) solutions of these complexes, recorded on a UVISPEK spectrophotometer, exhibited \(\lambda_{\text{max}}\) at 490 nm, similar to that reported in literatures\(^16\)\(^,\)\(^17\). The absorption spectra of 1:1, 1:2 and 1:3 mixtures (complex: incoming ligand; complex concentration being 0.005 mol dm\(^{-3}\)) for both the systems thermostated at 45°C for 48 hr at pH 4.0 exhibited \(\lambda_{\text{max}}\) at 490 nm. The products of the reactions of \([\text{Co(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) and \([\text{Cr(BigH)}_2(\text{H}_2\text{O})_2]^{2+}\) with histidine were prepared by mixing the reactants in 1:1 molar ratio and the reaction mixtures refluxed for 48 hr on a water-bath. Solid products separated out on concentration of reaction mixtures. The elemental analyses of isolated products revealed the compositions \([\text{Co(BigH)}_2(\text{Hist.H})]^{3+}\) and \([\text{Cr(BigH)}_2(\text{Hist.H})]^{3+}\) (Complex-II). Further these complexes exhibited \(\lambda_{\text{max}}\) at 490 nm.

In all experiments AR grade chemicals were used and doubly distilled water was used for preparing solution. All measurements were made on a Hilger UVISPEK spectrophotometer at 460 nm where the absorptions of the reacting complexes and the...
plexes formed as products differ appreciably. Temperature equilibrated solutions of histidine and the Complex-I were mixed and the concentrations of the reactants in the experimental solutions were such that the first order rate law were applicable and the pseudo-first order rate constants, \( k_{\text{obs}} \), for each experiment were evaluated graphically by plotting \( \log(D_{\text{in}} - D_{\text{f}}) / (D_{\text{in}} - D_{\text{f}})(t) \) versus time \( t \), where \( D_{\text{in}}, D_{\text{f}} \), and \( D_{\text{f}} \) are the absorbances at infinite time, in the beginning and after time, \( t \), respectively. Rates are reproducible within ±3%.

**Results and Discussion**

(i) **Effect of varying [Complex-I] on rate constants**

In the set of experiments performed at 45°C the [Complex-I] was varied from 0.005 mol dm\(^{-3}\) to 0.0075 mol dm\(^{-3}\) at fixed [histidine] of 0.1 mol dm\(^{-3}\), \( pH = 4 \) and ionic strength (I) = 0.5 mol dm\(^{-3}\). The pseudo-first order rate constant \( (k_{\text{obs}}) \) for anation of \([\text{Co}(\text{BigH})_2(\text{H}_2\text{O})_2]\)\(^3+\) was \((1.4 ± 0.04) \times 10^{-4} \) s\(^{-1}\) that for \([\text{Cr}(\text{BigH})_2(\text{H}_2\text{O})_2]\)\(^3+\) it was \((4.0 ± 0.2) \times 10^{-4} \) s\(^{-1}\). The \( k_{\text{obs}} \) values were found to be in good agreement with the first order rate law:

\[
\frac{d[\text{Complex-II}]}{dt} = k_{\text{obs}}[\text{Complex-I}]
\]

(ii) **Effect of varying [histidine] on rate constant**

The [histidine] was varied in the range of 0.05 to 0.15 mol dm\(^{-3}\) at fixed [Complex-I] = 0.005 mol dm\(^{-3}\), \( pH = 4 \) and ionic strength (I) = 0.5 mol dm\(^{-3}\) for both the systems. The results presented in (Table 1) show that the rates increase with increase in [Hist.H\(^+_2\)] and approach a limiting rate at higher [Hist.H\(^+_2\)] (Figs. 1a, 1b) for both the systems. This behaviour may be due to completion of ion-pair formation at higher [Hist.H\(^+_2\)] (ref. 18).

The above results lead to Scheme 1 as a plausible mechanism for anation at different concentrations of the incoming ligand. Scheme 1 leads to rate law (1)

\[
\text{cis-}[\text{M}(\text{BigH})_2(\text{H}_2\text{O})_2]\]\(^3+\) + Hist.H\(^+_2\) \rightarrow \text{cis-}[\text{M}(\text{BigH})_2(\text{H}_2\text{O})_2]^{2+}\text{Hist.H}\]\(^+\)

\[\text{[M = Co(II) and Cr(III)]} \tag{1P}\]

\[
\frac{d[\text{M}(\text{BigH})_2(\text{H}_2\text{O})_2]\]^{3+}\text{Hist.H}\]\(^+\) \rightarrow \text{Slow} \rightarrow [\text{M}(\text{BigH})_2(\text{Hist.H})]^{3+} + \text{H}_2\text{O} + \text{H}^+

\text{Scheme 1}

\[
\frac{d[\text{M}(\text{BigH})_2(\text{Hist.H})]^{3+}}{dt} = k_1k_2[E[\text{M}(\text{BigH})_2(\text{H}_2\text{O})_2]^3+]_{\text{total}} [\text{Hist.H}]^+ \tag{11}
\]

\[
= k_{\text{obs}}[\text{M}(\text{BigH})_2(\text{Hist.H})]^{3+}_{\text{total}} \tag{2}
\]

Table 1 – Variation of Rate Constant \( (k_{\text{obs}}) \) with [Hist.H\(^+_2\)] at Different Temperatures

<table>
<thead>
<tr>
<th>[Hist.H(^+_2)]</th>
<th>( k_{\text{obs}} \times 10^4 ) S(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.41</td>
</tr>
<tr>
<td>0.075</td>
<td>0.57</td>
</tr>
<tr>
<td>0.100</td>
<td>0.72</td>
</tr>
<tr>
<td>0.125</td>
<td>0.84</td>
</tr>
<tr>
<td>0.150</td>
<td>0.95</td>
</tr>
<tr>
<td>0.200</td>
<td>1.02</td>
</tr>
<tr>
<td>0.250</td>
<td>1.09</td>
</tr>
<tr>
<td>0.300</td>
<td>1.19</td>
</tr>
<tr>
<td>0.350</td>
<td>1.38</td>
</tr>
<tr>
<td>0.400</td>
<td>1.76</td>
</tr>
<tr>
<td>0.450</td>
<td>2.13</td>
</tr>
<tr>
<td>0.500</td>
<td>2.71</td>
</tr>
<tr>
<td>0.550</td>
<td>3.36</td>
</tr>
<tr>
<td>0.600</td>
<td>4.02</td>
</tr>
</tbody>
</table>

Fig. 1 – Plot of \( k_{\text{obs}} \) versus [ligand] at different temperatures [(a) Co\(^{III}\) system and (b) Cr\(^{III}\) system]
Equation (4) implies that the plot of $1/k_{obs}$ versus $1/[\text{Hist.H}^+]$ should be linear. This actually found to be so in both the cases (Figs. 2a, 2b). From such linear plots $k_a$ values (Table 2) and $K_E$ values were obtained from the intercept $1/k_a$ and slope $1/k_a K_E$ respectively. The $K_E$ values of cis-[Co(BigH$_3$(H$_2$O)$_2$]$^3^+$ and cis-[Cr(BigH$_3$(H$_2$O)$_2$]$^3^+$ are almost constants and are in the range of 5.2 to 7.1 and 4.5 to 8.0 respectively.

(iii) Effect of varying pH on rate constant

Under the condition; [Complex-I] = 0.005 mol dm$^{-3}$; [Hist.H$^+$] = 0.1 mol dm$^{-3}$; ionic strength = 0.5 mol dm$^{-3}$; and temp. = 45°C the pH of the medium was varied in the range of 3.85 to 5.57 [pH were adjusted by adding NaOH or HClO$_4$] in both the cases. It was observed that, $k_{obs}$ values for the anation of [Co(BigH$_3$(H$_2$O)$_2$]$^3^+$ were $1.32 \times 10^{-4}$, $1.42 \times 10^{-4}$, $1.63 \times 10^{-4}$, $1.92 \times 10^{-4}$, $2.20 \times 10^{-4}$, $2.8 \times 10^{-4}$ s$^{-1}$ and for [Cr(BigH$_3$(H$_2$O)$_2$]$^3^+$ the $k_{obs}$ values were $3.6 \times 10^{-4}$, $3.8 \times 10^{-4}$, $4.1 \times 10^{-4}$, $4.6 \times 10^{-4}$, $5.5 \times 10^{-4}$ and $5.9 \times 10^{-4}$ s$^{-1}$ at pH 3.85, 4.0, 4.47, 4.89, 5.32 and 5.57 respectively. Here we find that the $k_{obs}$ values increase with increase the pH of the medium. This can be explained as follows:

In the above mentioned pH range the ligand histidine comes as a positive charge in solution because it dissociates as shown in Scheme 2. So the change in pH does not alter the ligand reactivity considerably. Let us consider the acid dissociation equilibria of both the complexes (Eqs 5 and 6).

$$K_1 \text{cis-[Co(BigH}_3(H_2O)_2]^3^+ \rightleftharpoons \text{cis-[Co(BigH)}_2(\text{OH})_(H_2O)]^2^+ + H^+ \quad \ldots \ldots \ldots \ldots (5)$$

Table 2 - Values of $k_a$ for the Anation of [Complex-I] by Histidine at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$M=$Co$^{III}$</th>
<th>$M=$Cr$^{III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>8.33</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>9.52</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>10.70</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>12.12</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>12.12</td>
<td></td>
</tr>
</tbody>
</table>

The $pK_1$ value for the first case is observed$^{16}$ to be 6. But for second case the $pK_1$ value, determined $pK_1$-
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Conclusion

The results obtained in the present study suggest that the reactions between $[M(BigH)_{2}(H_{2}O)]^{3+}$ with histidine involve outer sphere association between the two reacting species followed by an associative interchange process where both bond breaking and bond making occur in a concerted manner. Generally substitution of aquo ligands from Co(III) aquo complexes proceed through dissociative pathway. But in the ana-
mechanism was suggested. For this case also $\Delta H^{\ddagger}$ value is quite low and a large negative $\Delta S^{\ddagger}$ is noticed indicating a significant ligand participation in the transition state. Considering all the results an associative interchange (Ia) mechanism is suggested for the replacement reaction of aquo ligands of $[Cr(BigH)_{2}(H_{2}O)]^{3+}$ by histidine.

The activation parameters for $[Cr(BigH)_{2}(H_{2}O)]^{3+}$ + histidine have been compared with the activation parameters for the substitution of aquo ligands of this complex by neutral ligands like 2,2'-dipyridyl and 1,10-phenanthroline. Earlier authors observed high activation energy for such systems and suggested an Ia mechanism. But in the present system the $\Delta H^{\ddagger}$ value is quite low while $\Delta S^{\ddagger}$ is large and negative. This indicates significant ligand participation in the transition state. Considering all the results an associative interchange (Ia) mechanism is suggested for the replacement reaction of aquo ligands of $[Cr(BigH)_{2}(H_{2}O)]^{3+}$ by histidine.

(iv) Effect of temperature on reaction rate

The reactions for both the cases were studied at four different temperatures at different [ligand] and the values of the rate constants for interchange processes are given in Table 1. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) of the two systems were evaluated from the linear Eyring plots of log $k_a$ versus 1/T. For $cis-[Co(BigH)_{2}(H_{2}O)]^{3+}$ the $\Delta H^{\ddagger}$ value is found to be $(43.41 \pm 2.09)$ kJ mol$^{-1}$ and $\Delta S^{\ddagger}$ value is $(-171.24 \pm 2.09)$ JK$^{-1}$ mol$^{-1}$ and for $cis-[Cr(BigH)_{2}(H_{2}O)]^{3+}$ the corresponding values are $(26.37 \pm 2.303)$ kJ mol$^{-1}$ and $(-215.78 \pm 2.09)$ JK$^{-1}$ mol$^{-1}$. In both the cases we obtain low $\Delta H^{\ddagger}$ values and large negative $\Delta S^{\ddagger}$ values. The activation parameters thus determined are presented in Table 3.

The activation parameters for $[Co(BigH)_{2}(H_{2}O)]^{3+}$ + histidine system are compared with activation parameters for substitution of aquo ligands of the Co(III) system by phenylbiguanide as given by Chakravorty and Sil. The authors observed low activation energy for the system showed by them and suggested Ia mechanism. These activation parameter values obtain by us have also been compared with activation parameters for substitution of aquo ligands of the Cr(III) system by phenylalanine where also a low $\Delta H^{\ddagger}$ value and a large negative $\Delta S^{\ddagger}$ value were observed and an Ia mechanism was suggested. For this case also $\Delta H^{\ddagger}$ value is quite low and a large negative $\Delta S^{\ddagger}$ is noticed indicating a significant ligand participation in the transition state. Considering all the results an associative interchange (Ia) mechanism is suggested for the replacement reaction of aquo ligands of $cis-[Co(BigH)_{2}(H_{2}O)]^{3+}$ by histidine.

Table 3 - Activation Parameters

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta H^{\ddagger}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^{\ddagger}$ (JK$^{-1}$ mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$cis-[Co(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + histidine</td>
<td>$43.41 \pm 2.09$</td>
<td>$-171.24 \pm 2.09$</td>
<td>This work</td>
</tr>
<tr>
<td>$cis-[Co(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + phenylbiguanide</td>
<td>57.78</td>
<td>$-83.74$</td>
<td>16</td>
</tr>
<tr>
<td>$cis-[Co(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + phenylalanine</td>
<td>45.97</td>
<td>$-162.03 \pm 2.09$</td>
<td>19</td>
</tr>
<tr>
<td>$cis-[Cr(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + histidine</td>
<td>$26.37 \pm 2.303$</td>
<td>$-215.78 \pm 2.09$</td>
<td>This work</td>
</tr>
<tr>
<td>$cis-[Cr(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + 2,2'-dipyridyl</td>
<td>85.82</td>
<td>$2.93$</td>
<td>17</td>
</tr>
<tr>
<td>$cis-[Cr(BigH)<em>{2}(H</em>{2}O)]^{3+}$ + 1,10-phenanthroline</td>
<td>82.89</td>
<td>$-3.34$</td>
<td>17</td>
</tr>
</tbody>
</table>

Scheme 3 - Probable mechanism for anation process

Effect of temperature on reaction rate

The reactions for both the cases were studied at four different temperatures at different [ligand] and the values of the rate constants for interchange processes are given in Table 1. Activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) of the two systems were evaluated from the linear Eyring plots of log $k_a$ versus 1/T. For $cis-[Co(BigH)_{2}(H_{2}O)]^{3+}$ the $\Delta H^{\ddagger}$ value is found to be $(43.41 \pm 2.09)$ kJ mol$^{-1}$ and $\Delta S^{\ddagger}$ value is $(-171.24 \pm 2.09)$ JK$^{-1}$ mol$^{-1}$ and for $cis-[Cr(BigH)_{2}(H_{2}O)]^{3+}$ the corresponding values are $(26.37 \pm 2.303)$ kJ mol$^{-1}$ and $(-215.78 \pm 2.09)$ JK$^{-1}$ mol$^{-1}$. In both the cases we obtain low $\Delta H^{\ddagger}$ values and large negative $\Delta S^{\ddagger}$ values. The activation parameters thus determined are presented in Table 3.

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The activation parameters for $[Cr(BigH)_{2}(H_{2}O)]^{3+}$ + histidine have been compared with the activation parameters for the substitution of aquo ligands of this complex by neutral ligands like 2,2'-dipyridyl and 1,10-phenanthroline. Earlier authors observed high activation energy for such systems and suggested an Ia mechanism. But in the present system the $\Delta H^{\ddagger}$ value is quite low while $\Delta S^{\ddagger}$ is large and negative. This indicates significant ligand participation in the transition state. Considering all the results an associative interchange (Ia) mechanism is suggested for the replacement reaction of aquo ligands of $cis-[Cr(BigH)_{2}(H_{2}O)]^{3+}$ by histidine.

Conclusion

The results obtained in the present study suggest that the reactions between $[M(BigH)_{2}(H_{2}O)]^{3+}$ with histidine involve outer sphere association between the two reacting species followed by an associative interchange process where both bond breaking and bond making occur in a concerted manner. Generally substitution of aquo ligands from Co(III) aquo complexes proceed through dissociative pathway. But in the ana-
tion of [Co(BigH)\(_2\)(H\(_2\)O\(_2\)]\(^{3+}\) by histidine, a low \(\Delta H^+\) and a negative \(\Delta S^+\) prompted us to invoke an associative interchange mechanism. The following argument can be given as an explanation for such observation. Biguanide itself is an unsaturated ligand and has a \(\pi\)-back bonding tendency. It is likely that the \(\pi\)-bonding of the bischelate ligand removes electron cloud around cobalt and chromium centres from \(t_{2g}\) orbitals, thereby increasing the tendency of these orbitals to accept the incoming ligand. Therefore, significant bond formation takes place before any bond breakage in the transition state. In the present systems such a mechanism is supported by the low \(\Delta H^+\) values, because the energy of the bond breaking is partially compensated by the energy released due to the bond formation by the incoming ligand. The probable scheme of the reaction is drawn in Scheme 3. A compact associated transition state is produced by the ion-pair formation between Complex-I and ligand by \(\text{H-bonding as shown in Scheme 3.}

References