Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. XI. Water Exchange of cis- and trans-Tetraamminediaqua-, of fac-Triamminetriaqua- and of trans-Diamminetetraaquachromium(III) Ions in Aqueous Perchloric Acid

L. MONSEN and O. MØNSTED

Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Water exchange of cis- and trans-tetraamminediaqua-, of fac-triaminetriaqua- and of trans-diamminetetraaquachromium(III) in a 1 M perchlorate medium has been investigated. Rate constants at 25 °C for the exchange of one water ligand and activation energies are:

cis-[Cr(NH₃)₄(OH₂)₂]³⁺: 
(5.92 ± 0.13) × 10⁻⁵ s⁻¹, 95.1 ± 1.9 kJ mol⁻¹;
trans-[Cr(NH₃)₄(OH₂)₂]³⁺: 
(1.17 ± 0.03) × 10⁻⁵ s⁻¹, 98.5 ± 2.1 kJ mol⁻¹;
fac-[Cr(NH₃)₃(OH₂)₁]³⁺: 
(5.78 ± 0.09) × 10⁻⁵ s⁻¹, 95.1 ± 1.3 kJ mol⁻¹;
trans-[Cr(NH₃)₃(OH₂)₁]³⁺: 
(0.997 ± 0.013) × 10⁻⁵ s⁻¹, 97.0 ± 1.1 kJ mol⁻¹.

The rate constants correlate well with data for aquation of ammine- and halogenidochromium(III) complexes, and for a fixed set of non-reacting ligands the following relative aquation rates have been estimated for five series of complexes:

17(I⁻) : 1.5(Br⁻) : 1(OH⁻) : 1/11(Cl⁻) : 1/280 (NCS⁻) : 1/1400 (NH₃).

The kinetics of configurational changes of chromium(III) complexes have not been widely investigated. Recently we presented some indirect evidence in favour of the importance of water exchange for the occurrence of trans to cis isomerization of the chloride ligands in ammineaquachloridochromium(III) complexes. More direct evidence will have to come from quantitative data for water exchange and in the present work results for cis- and trans-tetraamminediaqua-, fac-triaminetriaqua- and trans-diamminetetraaquachromium(III) are reported. When combined with literature data for pentaaquamineaqua-² and hexaaquachromium(III)³ this completes the series of ammineaquachromium(III) ions with equivalently coordinated water ligands.

EXPERIMENTAL

Chemicals. [Cr(NH₃)₃Br]Br₄,⁴ cis-[Cr(NH₃)₃Cl₂]-ClH₂O,⁵ trans-[Cr(NH₃)₃Br₂]BrH₂O,⁶ and trans-[Cr(NH₃)₃(OH₂)₂Cl₂]Cl₇ were prepared by literature methods. Fac-[Cr(NH₃)₃Cl₃] was obtained from Dr. P. Andersen.⁸ Ag(tos)* was prepared by the addition of p-toluenesulfonic acid to an aqueous solution of AgNO₃. The precipitate thus obtained was recrystallized twice from water, and dried in vacuum over solid NaOH. H₂¹⁸O (I.P. ~ 99 %) was obtained from 'Alfa products'. The source of other chemicals has been described earlier.⁹

Preparation of oxygen-1⁸ enriched aquachromium(III) complexes. 0.6 mmol of [Cr(NH₃)₃Br]Br₂ was treated with 1.9 mmol Ag(tos) in 1.0 ml H₂¹⁸O for 15 min at 30 °C. The reaction mixture was then frozen and excess H₂¹⁸O removed by sublimation in vacuum. The remaining solid, which is a mixture of chromium(III) complexes, AgBr and

* tos = p-toluensulfonate ≡ p-CH₃C₆H₄SO⁻₃.
unreacted excess Ag(tos), was treated with 0.01 M HClO₄ and excess Ag⁺ precipitated by addition of a concentrated solution of NaBr. AgBr was filtered off and the filtrate was charged onto a 10 cm × 2 cm column of Sephadex SP-C-25. Elution with 0.35 M NaClO₄, pH ~ 2, removed halogenido- and p-toluenesulfonate complexes, after which the oxygen-18 enriched pentaammineaquachromium(III) ion was eluted with 1.0 M NaClO₄, pH ~ 2. The eluate, about 25 ml, was diluted with the appropriate amount of 1.0 M (Na, H)ClO₄ and immediately used for the kinetic experiments.

* cis- and trans-[Cr(NH₃)₄(OH₂)₂]³⁺, fac-[Cr(NH₃)₃(OH₂)Br]⁺ and trans-[Cr(NH₃)₃(OH₂)Cl]⁺ were prepared analogously from *cis-[Cr(NH₃)₄Cl]⁺, ClH₂O, trans-[Cr(NH₃)₃Br₂]Br.H₂O, fac-[Cr(NH₃)₃Cl]⁺ and trans-[Cr(NH₃)₃(OH₂)Cl]₂Cl, respectively. In all cases, an amount of complex which, when dried at 100 °C, contained 0.6 mmol of coordinated halogenide ions was employed. All manipulations of oxygen-18 enriched complexes, including the ion exchange separations were carried out in the dark and at temperatures below 5 °C in order to minimize water exchange prior to the kinetic runs. The ammineaquacomplexes thus prepared had spectral characteristics in complete agreement with those of ammineaquachromium(III) complexes prepared and purified by other methods.

**Kinetic measurements.** Solutions prepared as described above were protected from light and placed in a thermostatted water bath maintained at the desired reaction temperature with an accuracy of ±0.05 °C. 10 ml samples were withdrawn at suitable time intervals and rapidly frozen. They were next sublimed in vacuum to yield about 8 ml of slightly acid water, pH ~ 5, which was used for the mass spectrometric ¹⁸O/¹⁶O ratio determinations. The residue from the sublimation was diluted to 10 ml with water and checked spectrophotometrically to see that loss of coordinated ammonia had not occurred.

**Methods of analyses** and spectrophotometric measurements have been described earlier.

**Mass spectrometric measurements.** The mass spectrometric measurements of the ¹⁸O/¹⁶O ratios, Rsample, were performed relative to V-SMOW (Vienna Standard Mean Ocean Water) at the Geophysical Isotope Laboratory at the University of Copenhagen. The results are given as δ-values, defined according to:

\[
\delta = (R_{\text{sample}} - R_{\text{V-SMOW}})/R_{\text{V-SMOW}}
\]

and the absolute ¹⁸O/¹⁶O ratio of V-SMOW: R⁰V-SMOW, has been found to have the value (205.20 ± 0.45) × 10⁻⁶. Experimental the δ-values are measured most accurately when close to 0. In the present investigation they were limited to the range from −15 ‰ to +30 ‰. At 0 °C (H₂¹⁸O)/ (H₂¹⁶O) ~ 1.018 and it is, therefore, important that all sublimations to yield the samples for the mass spectrometric measurements are carried out reproducibly. The major source of uncertainty was found to arise from small differences in the amount

---

**Fig. 1.** Reaction kinetic experiments for water exchange in fac-triaminetriaquachromium(III). The experimental points, ○, have been corrected for differences in the amount of sublimed water; cf. eqn. (1). The solid curves have been calculated from the rate parameters of Table 2.

of sublimed water and an empirical correction to the measured δ-values, \( \delta_{\text{corr}} \), as function of the volume of sublimed water, \( v \), had to be used. The correction was obtained from data for about 100 samples, and could be expressed as:

\[
\delta_{\text{corr}} \sim \frac{\delta_{\text{meas}}}{[1.22 + 1.82(\exp(-1.56(8.75-v)) - 1)]^{\gamma_{\text{corr}}}}
\]

valid for 7 ml \( \leq v \leq 9 \) ml of sublimed water.

Method of calculation. The corrected \( \delta \)-values, \( \delta_{\text{corr}} \), as function of time, \( t \), were approximated by a curve calculated from the expression:

\[
\delta_t = \delta_0 + \delta_c[\exp(-kt) - 1]
\]

(cf. the Appendix) with the three parameters: \( \delta_0 \), \( \delta_c \) and \( k \) estimated by minimization of:

\[
\sum_{t} (\delta_{\text{t,corr}} - \delta_t)^2 / \sigma^2(\delta_{\text{corr}})
\]

by non-linear regression analysis. \( \sigma^2(\delta_{\text{corr},t}) \) is the variance of \( \delta_{\text{corr},t} \). Some examples of the agreement between calculated curves and the experimental data are shown in Fig. 1. The further calculations to yield activation parameters were carried out essentially as described earlier.\(^1\)\(^2\)

RESULTS AND DISCUSSION

Oxygen-18 enriched ammineaqua chromium(III) complexes are most conveniently prepared by

Table 1. Comparison with literature values of some rate constants for water exchange.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. [°C]</th>
<th>([\text{H}^+]) [M]</th>
<th>[Cr(III)] [mM]</th>
<th>([18\text{O}]<em>{\text{Cr}}/\text{O}</em>{\text{aq}}) [%]</th>
<th>(10^5 k) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr(OH}_2\text{)}_4]^{3+})</td>
<td>39.8</td>
<td>2.06 ± 0.11</td>
<td>1.65 ± 0.5</td>
<td>-</td>
<td>2.11 ± 0.11</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>25.1</td>
<td>5.4 ± 0.3</td>
<td>2.49</td>
<td>0.50</td>
<td>5.9</td>
</tr>
</tbody>
</table>

*See appendix.*

Hydrolysis of Cr(III) Complexes XI

Table 2. Rate constants for water exchange in ammineaqua chromium(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp. [°C]</th>
<th>([\text{H}^+]) [M]</th>
<th>[Cr(III)] [mM]</th>
<th>([18\text{O}]<em>{\text{Cr}}/\text{O}</em>{\text{aq}}) [%]</th>
<th>(10^5 k) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>15.7</td>
<td>0.51</td>
<td>3.28</td>
<td>88</td>
<td>1.55 ± 0.09</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>25.6</td>
<td>0.51</td>
<td>3.13</td>
<td>87</td>
<td>6.23 ± 0.06</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>34.8</td>
<td>0.51</td>
<td>3.58</td>
<td>88</td>
<td>21.8 ± 0.4</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>15.3</td>
<td>0.51</td>
<td>3.23</td>
<td>50</td>
<td>1.62 ± 0.07</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>25.6</td>
<td>0.51</td>
<td>2.06</td>
<td>49</td>
<td>6.0 ± 0.3</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>35.2</td>
<td>0.50</td>
<td>2.11</td>
<td>50</td>
<td>22.9 ± 1.3</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>36.1</td>
<td>0.51</td>
<td>2.46</td>
<td>49</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>15.0</td>
<td>0.52</td>
<td>1.60</td>
<td>50</td>
<td>0.316 ± 0.019</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>19.9</td>
<td>0.52</td>
<td>1.86</td>
<td>48</td>
<td>0.63 ± 0.02</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>30.1</td>
<td>0.51</td>
<td>2.08</td>
<td>52</td>
<td>2.31 ± 0.07</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>30.3</td>
<td>0.22</td>
<td>1.87</td>
<td>51</td>
<td>2.17 ± 0.04</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>40.5</td>
<td>0.52</td>
<td>2.11</td>
<td>55</td>
<td>9.13 ± 0.17</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>14.9</td>
<td>0.52</td>
<td>1.39</td>
<td>80</td>
<td>1.49 ± 0.04</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>25.1</td>
<td>0.52</td>
<td>1.44</td>
<td>81</td>
<td>5.69 ± 0.12</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>35.3</td>
<td>0.53</td>
<td>1.45</td>
<td>86</td>
<td>21.0 ± 0.3</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>15.1</td>
<td>0.51</td>
<td>1.57</td>
<td>49</td>
<td>0.252 ± 0.005</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>24.9</td>
<td>0.52</td>
<td>1.03</td>
<td>56</td>
<td>1.00 ± 0.04</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3\text{)}_2\text{OH}_2\text{]}^{3+})</td>
<td>35.1</td>
<td>0.50</td>
<td>1.12</td>
<td>46</td>
<td>3.70 ± 0.08</td>
</tr>
</tbody>
</table>

the aquacomplexes by the ion exchange chromatographic procedure used to purify the aqua complexes.

The oxygen-18 labelled complexes were prepared from oxygen-18 labelled water which initially had an isotopic purity of about 99 %. After purification the isotopic oxygen-18 purity of the aqua complexes is somewhat lower, but approximately constant for individual complexes. This is shown in Table 2 where the isotopic purity is seen to be: ~90 % for the pentaammin-, ~50 % for both the cis- and the trans-tetraammine- and ~85 % for the fac-triimine complex. The cis- and trans-tetrammine-dihoalogenidochromium(III) starting materials may contain some aquahalogenido complex and this can also be formed during the heating of the complexes to remove water of crystallization. The pentaammineaque- and the fac-triimmineteraqua- chromium(III) are, however, prepared from nonhydrated starting materials. At 5 °C the half life for water exchange in all the ammineaquachromium(III) complexes is greater than 30 h. Preparation of the reactant solutions usually took about 2–3 h and the lowering of the isotopic purity of the generated ammineaquachromium(III) complexes compared to that of the reactant water can, therefore, most likely be attributed to the kinetic significance of deprotonated complexes at pH ~2 the condition under which most manipulations, including the ion exchange separation, were carried out; cf. Ref. 16. trans-Diamineteraqua chromium(III) is generated from a complex ion which already contains two water ligands of normal isotopic distribution. This ion is seen to have an isotopic purity of about 50 % and, therefore, in this case some equilibrium between solvent and coordinated water must have taken place during the preparation.

Slow water exchange reactions of metal complexes are usually studied by oxygen-18 labelling and mass spectrometric monitoring of the $^{16}$O/$^{18}$O ratio in the complex or solvent after separation, usually by precipitation of the complex. For the ammineaquachromium(III) complexes this approach is, however, not generally applicable and it was, therefore, necessary to modify established methods. This included the use of complexes, highly labelled in oxygen-18,

![Fig. 2. Comparison with literature data of the rate of water exchange in pentamminewater chromium(III). The experimental points have been drawn with a vertical extent corresponding to ±1 × the estimated standard deviations. The solid line is the basis for the parameters of Table 3.](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$10^2 k$(25 °C) $[s^{-1}]$</th>
<th>$\Delta H^*$ $[kJ \text{ mol}^{-1}]$</th>
<th>$\Delta S^*$ $[J K^{-1} \text{ mol}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(NH$_3$)$_5$(OH$_2$)$_2$]$^{3+}$</td>
<td>5.75 ± 0.06</td>
<td>99.1 ± 1.4</td>
<td>+7 ± 5</td>
</tr>
<tr>
<td>cis-[Cr(NH$_3$)$_4$(OH)$_2$]$^{3+}$</td>
<td>5.92 ± 0.13</td>
<td>95.1 ± 1.9</td>
<td>-7 ± 6</td>
</tr>
<tr>
<td>trans-[Cr(NH$_3$)$_4$(OH)$_2$]$^{3+}$</td>
<td>1.17 ± 0.03</td>
<td>98.5 ± 2.1</td>
<td>-9 ± 7</td>
</tr>
<tr>
<td>fac-[Cr(NH$_3$)$_3$(OH)$_2$]$^{3+}$</td>
<td>5.78 ± 0.09</td>
<td>95.1 ± 1.3</td>
<td>-7 ± 5</td>
</tr>
<tr>
<td>trans-[Cr(NH$_3$)$_2$(OH)$_2$]$^{3+}$</td>
<td>0.997 ± 0.013</td>
<td>97.0 ± 1.1</td>
<td>-15 ± 4</td>
</tr>
<tr>
<td>[Cr(OH$_2$)$_6$]$^{3+}$</td>
<td>0.246 ± 0.012</td>
<td>109.6 ± 1.3</td>
<td>+16 ± 5</td>
</tr>
</tbody>
</table>

* See appendix. $^b$ Ref. 2 and this work (see Fig. 2). $^c$ Ref. 3.
in combination with high precision mass-spectrometry. Ordinary water contains about 0.20 % of H$_2$O which is equivalent to a 111 mM solution. Changes of a few per cent of this value can be accurately measured, and this corresponds to changes in H$_2$O at the millimolar level; cf. Table 1. Fig. 1 shows some examples of kinetic runs, and in Table 1 and Fig. 2 are given comparisons of results obtained using this modified technique and earlier literature data for hexaaquachromium(III), pentaamineaquachromium(III) and -cobalt(III), all of which were studied by monitoring the oxygen-18 content in the complex ion isolated by precipitation.

In Table 2 are shown data for water exchange of cis- and trans-tetraaminediaqua-, fac-triamine- 
triaqua- and trans-diaminitetraaquachromium- 
(III) in a 1 M perchlorate medium, and in Table 3 these data have been collected to give activation parameters for the reactions. The rate of water exchange of trans-tetraaminediaquachromium(III) is seen to be independent of the hydrogen ion concentration, and literature data in combination with the present data show that this is also the case for pentaamineaquachromium$^{2,16}$ and hexaaquachromium-(III)$^3$ at such high acidities as employed in this work. cis-Tetraaminediaqua-, fac-triamine- 
triaqua- and trans-diaminitetraaquachromium(III) have not been investigated at different hydrogen ion concentrations but comparisons with the chromium(III) complexes cited above, which contain examples of water exchange trans to both ammonia and water, make it very likely that the measured rate constants should be attributed to an acid independent reaction.

Fig. 3 is a comparison of the results for a number of reactions of the type:

$$\text{CrL}_2X + \text{OH}_2 \rightarrow \text{CrL}_2\text{OH}_2 + X$$

(“CrL$_2$” = “Cr(NH$_3$)$_2$”), “cis-Cr(NH$_3$)$_2$(OH)$_2$”, “trans-Cr(NH$_3$)$_2$(OH)$_2$”, “fac-Cr(NH$_3$)$_2$(OH)$_2$” and “Cr(OH)$_2$”; X = I$^-$, Br$^-$, Cl$^-$, NCS$^-$, OH$_2$ and NH$_3$). The present data for X = OH$_2$ are in good agreement with those predicted on the basis of linear free energy relationships. The data exhibited on the figures accord with the division of $\Delta G^*$ for process (2) into two terms, depending on the non-reacting ligands and the leaving ligand, respectively:

$$\Delta G^* \sim \Delta G^*(\text{CrL}_2) + \Delta G_X^*$$

A summary of the data obtained using this equation is given in Table 4.

Fig. 3 clearly demonstrates the larger kinetic trans effect of coordinated ammonia compared to coordinated water and a further discussion of this and also of the significantly smaller kinetic cis effect of these two ligands will be given by us in combination with the presentation of results for those ammineaquachromium(III) complex ions.

Table 4. Single ligand reactivity parameters, $\Delta G_X^*$, at 25 °C, for aquation of chromium(III) complexes, cf. eqn. (3) and Fig. 3, and the corresponding rate constant ratios.

<table>
<thead>
<tr>
<th>X</th>
<th>$\Delta G_X^* - \Delta G_{\text{OH}_2}^*$ [kJ mol$^{-1}$]</th>
<th>$k_X/k_{\text{OH}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^-$</td>
<td>-7</td>
<td>17</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>-1</td>
<td>1.5</td>
</tr>
<tr>
<td>OH$_2$</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>+6</td>
<td>1/11</td>
</tr>
<tr>
<td>NCS$^-$</td>
<td>+14</td>
<td>1/280</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>+18</td>
<td>1/1400</td>
</tr>
</tbody>
</table>
which contain non-equivalently coordinated water ligands. *i.e.* mer-triamminetriaqua- *cis*-diamminetetraaqua- and amminenpentaaquachromium(III).

**Acknowledgement.** The authors wish to thank the Geophysical Isotope Laboratory at the University of Copenhagen, particularly Dr. Niels Gundestrup, for carrying out the mass spectrometric analyses.

**APPENDIX**

In the discussion of the relative magnitude of rate constants, it is customary to apply statistical corrections when the reactivity of two or more equivalently coordinated ligands have been measured. The reaction scheme for substitution of two equivalently coordinated ligands by first order processes:

\[
\begin{align*}
L^*M L & \\
L^*M & \\
L^* & \\
M L &
\end{align*}
\]

allows, in principle, the estimation of two rate constants as all the concentration *vs.* time relationships can be expressed as linear combinations of three exponential functions: \( \exp(-2k't) \), \( \exp(-k''t) \) and \( \exp(0-t) \). This is, of course, well-known and the basis for the statistical correction with a factor 2 to \( k_{obs} = 2 k' \).

For an exchange process \( L = L^* \) and therefore \( k' = k'' \). For this type of process it is usually only possible to follow the concentration of label in either the solvent: \( [L^*] \), or the complex: \( [2[L^*ML^*]] + [LML^*] \), and neither of these concentrations contains any information about \( \exp(-2k't) \), as can be seen from a simple calculation, *viz.*:

\[
[L^*]_t = [L^*]_0 + 2[L^*ML^*]_0 + [LML^*]_0 \{1 - \exp(-k't)\}
\]

and analogously for \( 2[L^*ML^*] + [LML^*] \).

**Observed rate constants from this type of measurement should therefore not be corrected statistically.** This has not always been realized in the literature.

**REFERENCES**

8. Andersen, P. To be published.

Received December 19, 1979.