

# Kinetics of Water Exchange of *cis*- and *trans*-Tetraamminediaqua- and of *cis*- and *trans*-Tetraammineaquachloridorhodium(III). Kinetic *trans*-Effect Differences in Octahedral Substitution Reactions

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Water exchange of *cis*- and *trans*-tetraamminediaqua- and of *cis*- and *trans*-tetraammineaquachloridorhodium(III) in an acid 1 M perchlorate medium has been investigated. Rate constants at 25 °C for the exchange of *one* water ligand and activation energies are:

$$\textit{cis}\text{-}[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+} \\ (7.5 \pm 0.3) \times 10^{-6} \text{ s}^{-1} \quad 108.1 \pm 1.4 \text{ kJ mol}^{-1}$$

$$\textit{trans}\text{-}[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+} \\ (7.2 \pm 0.5) \times 10^{-9} \text{ s}^{-1} \quad 145.5 \pm 1.7 \text{ kJ mol}^{-1}$$

$$\textit{cis}\text{-}[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+} \\ (23.8 \pm 0.3) \times 10^{-6} \text{ s}^{-1} \quad 105.5 \pm 1.4 \text{ kJ mol}^{-1}$$

$$\textit{trans}\text{-}[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+} \\ (33.8 \pm 0.9) \times 10^{-6} \text{ s}^{-1} \quad 101.7 \pm 2.1 \text{ kJ mol}^{-1}$$

These data, in combination with literature data for water exchange in pentaammineaquarhodium(III) establish the kinetic *trans*-effect order, for a fixed set of *cis* ligands, as:



for substitution reactions at a rhodium(III) center. The much larger kinetic *trans* effect for rhodium(III) as compared to chromium(III) for the same *trans* ligand has been rationalized in terms of differences in ligand field stabilization energies.

A systematic study of the effect of non-reacting ligands on the rate of water exchange in the complete series of ammineaquachromium(III) complexes was recently shown to give detailed information on the stereochemistry of the transition states for these processes.<sup>1</sup> The model used to rationalize the kinetic *cis* effect for these reactions should in principle be able to account for important features of substitution reactions of metal ions in general, and in an attempt to further verify this hypothesis a study of water exchange in rhodium(III) complexes has been initiated. Data for the isomeric tetraamminediaqua- and tetraammineaquachloridorhodium(III) ions are reported here.

## RESULTS AND DISCUSSION

Oxygen-18 enriched aquarhodium(III) complexes are conveniently prepared by accelerated removal of chloride ligands using silver(I)tosylate in oxygen-18 enriched water, a method which has previously been used to prepare similarly labelled ammineaquachromium(III) complexes.<sup>2</sup> The processes are significantly slower for rhodium(III) than for chromium(III) and it is possible to prepare both tetraammineaquachlorido-<sup>3</sup> and tetraamminediaquarhodium(III) ions from the isomeric tetraamminedichloridorhodium(III) chloride salts.

Table 1. Rate constants for water exchange in some rhodium(III) complexes in 0.50 M HClO<sub>4</sub>+0.50 M NaClO<sub>4</sub>.

| Temp. [°C]   | Rh(III) [mM] | <sup>18</sup> O/Rh at <i>t</i> =0 | 10 <sup>5</sup> <i>k</i> [s <sup>-1</sup> ] |
|--|--------------|-----------------------------------|---|
| <i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup>   |              |                                   |   |
| 24.9 <sub>5</sub>  | ~2           | ~1.8                              | 45.1±1.6                                    |
| 35.0 <sub>5</sub>  | 1.80         | 1.82                              | 179±6                                       |
| 45.1 <sub>0</sub>  | 2.05         | 1.90                              | 703±7                                       |
| <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup> |              |                                   |   |
| 59.9 <sub>0</sub>  | 2.00         | 1.68                              | 20.5±0.2                                    |
| 69.5 <sub>0</sub>  | ~1.4         | ~1.8                              | 86±4  |
| 79.4 <sub>0</sub>  | 1.58         | 1.54                              | 379±13                                      |
| <i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> )Cl] <sup>2+</sup>               |              |                                   |   |
| 15.1 <sub>0</sub>  | 2.03         | 0.78                              | 32.9±1.6                                    |
| 24.9 <sub>5</sub>  | ~2           | ~0.8                              | 141±10                                      |
| 24.9 <sub>5</sub>  | 2.40         | 0.79                              | 146±9                                       |
| 34.9 <sub>5</sub>  | 1.90         | 0.90                              | 547±31                                      |
| <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> )Cl] <sup>2+</sup>             |              |                                   |   |
| 14.9 <sub>5</sub>  | 1.71         | 0.89                              | 48±3  |
| 24.9 <sub>5</sub>  | 2.20         | 0.83                              | 216±18                                      |
| 35.0 <sub>0</sub>  | 1.80         | 0.84                              | 764±23                                      |

The water exchange,  $\delta$ , as function of time,  $t$ , was monitored mass spectrometrically on the solvent water after separation from the dissolved salts. For all four complexes it was found accurately to follow a theoretical expression of the form expected for exchange of one type of water ligands, i.e.:

$$\delta_t = \delta_o + \delta_c(\exp(-kt) - 1)$$

where  $k$  is the rate constant for exchange of one water ligand.<sup>2</sup> A summary of the rate constants and the isotopic purity of the complexes at the start of the kinetic experiments is given in Table 1. This latter quantity is seen to be comparable to that of the reactant water, although slightly smaller for the *trans*-tetraamminediaquarhodium(III) ion, which was allowed a somewhat longer time for temperature equilibration. Table 2 shows activation parameters derived from the temperature dependence of the rate constants in Table 1. Examination of these data in combination with literature data for water exchange in the pentaammineaquarhodium(III)<sup>4</sup> ion reveals a very small kinetic *cis* effect but a much larger

Table 2. Kinetic parameters for exchange of one water ligand in some rhodium(III) complexes.

| Complex  | 10 <sup>6</sup> × <i>k</i> (25°C) [s <sup>-1</sup> ] | Δ <i>H</i> <sup>*</sup> [kJ mol <sup>-1</sup> ] | Δ <i>S</i> <sup>*</sup> [J mol <sup>-1</sup> K <sup>-1</sup> ] | Ref.      |
|--|--|---|--|-----------|
| [Rh(NH <sub>3</sub> ) <sub>5</sub> (OH <sub>2</sub> )] <sup>3+</sup>                             | 8.41±0.18  | 102.9±1.3                                       | + 3±5  | 4         |
| <i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup>   | 7.5±0.3  | 105.4±1.3                                       | +11±4  | This work |
| <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup> | 0.0072±0.0005  | 143.1±1.7                                       | +78±5  | This work |
| <i>cis</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> )Cl] <sup>2+</sup>               | 23.8±0.3   | 102.9±1.3                                       | +12±4  | This work |
| <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> )Cl] <sup>2+</sup>             | 33.8±0.9   | 99.2±2.0  | + 3±7  | This work |

Table 3. Comparison of free energies of activation at 25 °C for water exchange in some chromium(III) and rhodium(III) complexes.

| <i>trans</i> ligand | Cr(III) complex  | $\Delta G^*$ [kJ mol <sup>-1</sup> ] | Ref. | Rh(III) complex  | $\Delta G^*$ [kJ mol <sup>-1</sup> ] | Ref.      |
|---------------------|--|--------------------------------------|------|--|--------------------------------------|-----------|
| OH <sub>2</sub>     | [Cr(OH <sub>2</sub> ) <sub>6</sub> ] <sup>3+</sup>                   | 105.04 ± 0.12                        | 9    | <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup> | 119.50 ± 0.17                        | This work |
| NH <sub>3</sub>     | [Cr(OH <sub>2</sub> ) <sub>5</sub> (NH <sub>3</sub> )] <sup>3+</sup> | 99.0 ± 0.3                           | 1    | [Rh(NH <sub>3</sub> ) <sub>5</sub> (OH <sub>2</sub> )] <sup>3+</sup>                             | 102.00 ± 0.05                        | 4         |
| Cl <sup>-</sup>     | [Cr(OH <sub>2</sub> ) <sub>5</sub> Cl] <sup>2+</sup>                 | 98.9 ± 0.2                           | 10   | <i>trans</i> -[Rh(NH <sub>3</sub> ) <sub>4</sub> Cl(OH <sub>2</sub> )] <sup>2+</sup>             | 98.55 ± 0.07                         | This work |

kinetic *trans* effect.

For the present rhodium(III) substitution reactions the kinetic *trans* effect order for water exchange is seen to be:



This *trans* effect order is in agreement with literature results derived from halide substitution data in *trans*-tetraammine-<sup>5,6</sup> and *trans*-bis(1,2-ethanediamine)rhodium(III)<sup>6-8</sup> species, but is free from some of the ambiguities which arise in an interpretation of data for reactions with non-zero changes in free energy. The present kinetic *trans* effect order for water exchange in rhodium(III) complexes is qualitatively the same as that observed for water exchange in chromium(III), based upon data for water exchange in pentaquachromium(III) species,<sup>1,9-10</sup> but as demonstrated in Table 3 the effect is much smaller for chromium(III) than for rhodium(III).

The order of ligands in (1) cannot be correlated with the order of empirical values for  $\sigma$ - and  $\pi$ -bonding in chromium(III)<sup>11</sup> and rhodium(III),<sup>12</sup> but does follow the ligand order in the nephelauxetic series. The significantly larger effect for the low spin  $d^6$  configuration of rhodium(III) than for the  $d^3$  configuration of chromium(III) suggests, however, that ligand field effects are important for the metal ion dependent part of the *trans* effect.

Application of ligand field models to kinetic problems requires consideration of both the ground state and the transition state. Both pentaamminerhodium(III) complexes and pentaquachromium(III) complexes react by an associative interchange mechanism although, by current criteria, the rhodium(III) reactions are

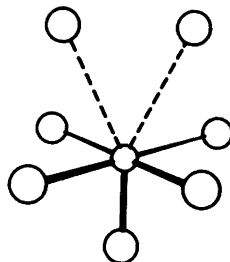


Fig. 1. Idealized transition state geometry used to rationalize kinetic *trans* effect differences between chromium(III) and rhodium(III).

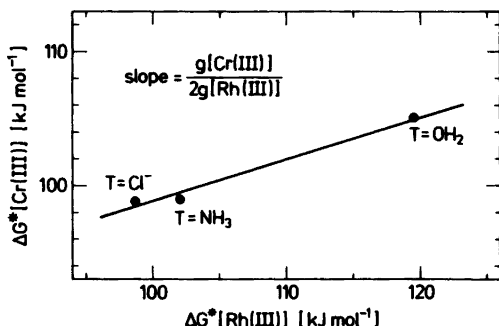


Fig. 2. Correlation between kinetic *trans* effect of water, ammonia and chloride in the chromium(III) and rhodium(III) complexes of Table 3. The straight line is drawn with a slope calculated from the non-kinetic *g*-parameters of Ref. 14:  $g[\text{Cr(III)}] \approx 208 \text{ kJ mol}^{-1}$  (17.4 kK) and  $g[\text{Rh(III)}] \approx 323 \text{ kJ mol}^{-1}$  (27.0 kK).

less associative than the chromium(III) reactions.<sup>13</sup> The transition state geometry shown in Fig. 1 has been used to rationalize ligand field effects of the substituted ligand for pentaqua- and pentaamminechromium(III) substitution reactions using angular overlap model calculations.<sup>14</sup> Similar calculations for rhodium(III) show that the contributions to the energy of activation from the *trans* ligand, T, in the two cases are given by eqns. (2a) and (2b):

$$\Delta L_{\text{T}[\text{Cr(III)}]}^* \approx \frac{1}{2}(\Delta_{\text{T}[\text{Cr(III)}]}^{\text{GS}} - \Delta_{\text{T}[\text{Cr(III)}]}^{\text{TS}}) \quad (2a)$$

$$\Delta L_{\text{T}[\text{Rh(III)}]}^* \approx \frac{2}{5}(\Delta_{\text{T}[\text{Rh(III)}]}^{\text{GS}} - \Delta_{\text{T}[\text{Rh(III)}]}^{\text{TS}}) \quad (2b)$$

The approximations inherent in eqns. 2a and 2b have been tested by angular overlap model calculations as demonstrated and documented in Ref. 14. For the  $d^3$  and  $d^6$  electronic configurations it has been verified that the contribution from the *trans* ligand to the overall ligand field stabilization energy is accurately given by  $-\frac{1}{2}\Delta_{\text{T}[\text{Cr(III)}]}$  and  $-\frac{2}{5}\Delta_{\text{T}[\text{Rh(III)}]}$ , respectively, both for the ground states and the transition states.

With the assumption that the relative change in the  $\Delta$ -parameter of the *trans* ligand when going from the ground state to the transition state is the same, and using the approximate separation of  $\Delta$  into a ligand and a metal dependent part<sup>15</sup>:

$$\Delta_{\text{T}[\text{M(III)}]} \approx f[\text{T}] \cdot g[\text{M(III)}]$$

eqns. 2 are easily transformed to give the *trans* ligand independent ratio:

$$\frac{\Delta L_{\text{T}[\text{Cr(III)}]}^*}{\Delta L_{\text{T}[\text{Rh(III)}]}^*} \approx \frac{g[\text{Cr(III)}]}{2g[\text{Rh(III)}]} \quad (3)$$

The validity of this approximation is tested in Fig. 2 and it is seen to describe rather well the metal ion dependent differences in kinetic *trans* effect between the present chromium(III) and rhodium(III) complexes.

Current views of the transition state as having less tightly bound ligands require the ligand field stabilization energies to be smaller in the transition state than in the ground state, which means that the present differences in kinetic *trans* effects are the result of a relatively smaller contribution to the ligand field stabilization of the transition state from the *trans* water ligand than from the *trans* ammonia and chloride ligands.

## EXPERIMENTAL

**Chemicals.** *Cis*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ <sup>16</sup> and *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ <sup>17</sup> were prepared by literature methods. The sources of other chemicals have been described previously.<sup>2</sup>

**Preparation of oxygen-18 enriched tetraammineaquachlorido- and tetraamminediaquarhodium(III) complexes.** Oxygen-18 enrichment of the rhodium(III) complexes was performed by the general method described earlier for robust chromium(III) complexes.<sup>2</sup> Specific details for the isomeric tetraammineaquachloridorhodium(III) species are given in Ref. 3. The tetraamminediaquarhodium(III) complexes were prepared analogously except for the employment of excess of silver(I) and different reaction times.

0.6 mmol of *trans*- $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$  was treated with 2.0 mmol  $\text{Ag}(\text{tos})$  ( $\text{tos} \equiv p$ -toluenesulfonate  $\equiv p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ) in 1.0 ml  $^{18}\text{OH}_2$  for 72 h at 70 °C. The reaction mixture was then frozen and excess water removed by sublimation in vacuum. The remaining solid, which is a mixture of rhodium(III) complexes,  $\text{AgCl}$  and unreacted  $\text{Ag}(\text{tos})$ , was treated with 0.01 M  $\text{HClO}_4$ , and excess  $\text{Ag}^+$  precipitated by addition of a concentrated solution of  $\text{NaBr}$ .  $\text{AgBr}$  and  $\text{AgCl}$  were filtered off and the filtrate was charged onto a 10 cm  $\times$  2 cm Sephadex SP-C-25 filled column. Elution with 0.25 M  $\text{NaClO}_4 + 0.01$  M  $\text{HClO}_4$  removed monovalent species and separated di- and trivalent species. These latter species were then eluted with 0.99 M  $\text{NaClO}_4 + 0.01$  M  $\text{HClO}_4$ , and the *trans*-

$[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$  eluate used for kinetic runs after dilution with the appropriate amount of  $(\text{Na,H})\text{ClO}_4$ .

*Cis*- $[\text{Rh}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$ -solutions were prepared analogously except for a reaction time at 70 °C of only 48 h.

*Kinetic measurements*,<sup>2</sup> *mass spectrometric measurements*,<sup>2</sup> *spectrophotometric measurements*,<sup>3</sup> *methods of analysis*<sup>2,3</sup> and *methods of calculation*<sup>2</sup> have all been described previously.

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