

# Reaction Rate Studies of the Acid Hydrolysis of Some Chromium(III) Complexes. XII. Water Exchange of *cis*-Diamminetetraaquachromium(III) in Aqueous Perchloric Acid

L. MØNSTED<sup>a</sup> and O. MØNSTED<sup>b</sup>

<sup>a</sup> Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark and <sup>b</sup> Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The rate of water exchange of *cis*-diamminetetraaquachromium(III) in an acid 1 M perchlorate medium has been investigated. The kinetics of this system is characterized by two first order processes, for which the rate constants at 25 °C and activation energies are:

1:  $(4.94 \pm 0.37) \times 10^{-5} \text{ s}^{-1}$ ,  $103.4 \pm 2.8 \text{ kJ mol}^{-1}$ ;  
2:  $(1.024 \pm 0.087) \times 10^{-5} \text{ s}^{-1}$ ,  $107.8 \pm 4.2 \text{ kJ mol}^{-1}$ .

Different methods of oxygen-18 labelling have allowed the estimation that the exchange process of both water ligand sites is largely stereoretentive, with the rate constant for the process which moves water ligands between the two sites less than  $(0.09 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$  at 25 °C. In less acid solution this latter type of isomerization is detectable and plays a significantly greater role.

Water exchange reactions of all ammineaquachromium(III) ions with equivalently coordinated water ligands, *i.e.* pentaammineaqua-, *cis*- and *trans*-tetraamminediaqua-, *fac*-triamminetriaqua-, *trans*-diamminetetraaqua- and hexaaquachromium(III) have earlier been investigated.<sup>1</sup> The kinetics of water exchange in aquaions with water ligands in different environments are more difficult to interpret in detail, and kinetic experiments have so far been limited to only the pentaquachlorido-, bromido-, iodido-, and -isothiocyanatochromium(III) cations.<sup>2,3</sup> The present work describes water exchange experiments with the *cis*-diamminetetraaquachromium(III) ion labelled with oxygen-18 at the two different water ligand sites.

## EXPERIMENTAL

**Chemicals.** *cis*-[Cr(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl was prepared according to Andersen and Berg.<sup>4</sup> The sources of other chemicals have been described previously.<sup>1</sup>

**Preparation of oxygen-18 labelled *cis*-diamminetetraaquachromium(III).** This cation was labelled with oxygen-18 enriched water either by removal of the chloride ligands or by equilibration of the water ligands in *cis*-diammine-*cis*-diaqua-*trans*-dichloridochromium(III), or by a combination of these two methods. The experimental approach follows closely that used previously by us,<sup>1</sup> and the three different methods which were tried are schematically outlined in Fig. 1 and described in detail for some typical experiments below.

**Method A.** 70 mg *cis*-[Cr(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl + 300 mg Ag(tos)\* was reacted in 1.0 ml O<sup>18</sup>-enriched water, I. P. ~95 %, at 40 °C for 40 min. Excess water was removed by sublimation and the remaining solid dissolved in 0.01 M HClO<sub>4</sub>. Excess Ag(I) was precipitated by adding excess NaBr-solution, and the resulting *cis*-[Cr(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>]<sup>3+</sup>-solution was purified by cation exchange chromatography essentially as described in Ref. 1.

**Method B.** 90 mg *cis*-[Cr(NH<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl + 350 mg Ag(tos) was reacted at 25 °C in 1.0 ml O<sup>18</sup>-enriched water, I. P. ~95 %, which had been acidified, pH ~1, by the addition of solid *p*-toluenesulfonic acid. This accelerated removal of the chloride ligands turned out, however, to be a rather slow process, and it was therefore stopped after 20 min when about 90 % of the chromium was present as the monochlorido complex. Excess

\* tos ≡ *p*-toluenesulfonate ≡ *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>.

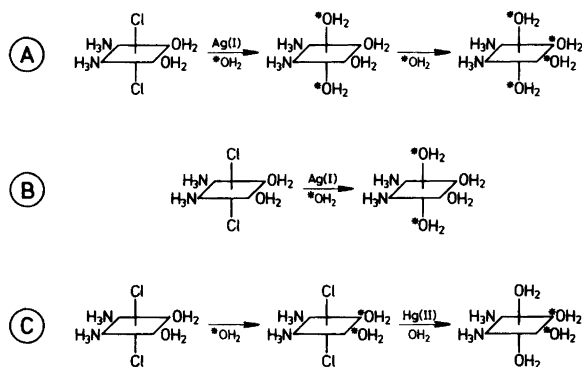


Fig. 1. Schematic drawing of different methods for oxygen-18 labelling *cis*-diamminetetraaqua chromium(III). Cf. the experimental section.

$\text{O}^{18}$ -water and Ag(I) was removed as described at method A, and the monochlorido complex was isolated by cation exchange chromatography by using a 15 cm  $\times$  2 cm Sephadex SP-C-25 filled column: The band of dipositive cations, *i.e.* the monochlorido- and small amounts of monotosylate complex, could be separated from other chromium species by elution with 0.4 M  $\text{NaClO}_4$ -solution at pH  $\sim$  2. The eluate, about 25 ml, containing the monochlorido complex was reacted with Hg(II) at pH  $\sim$  1. The production of the *cis*-diamminetetraaqua chromium(III) ion was followed spectrophotometrically, and was essentially quantitative within 5 min. Excess Hg(II)-aqua ions were complexed with  $\text{Br}^-$  and the resulting *cis*-diamminetetraaqua chromium(III) solution purified as described at method A.

*Method C.* 100 mg  $\text{cis-[Cr(NH}_3)_2(\text{OH}_2)_2\text{Cl}_2]\text{Cl}$  was aged in 1.0 ml of  $^{18}\text{O}$ -enriched water, I.P.  $\sim$  95 %, at pH  $\sim$  1 for 2 h at 25  $^\circ\text{C}$ . Under these conditions the half-life for release of the first chloride ligand is about 3.2 h.<sup>8</sup> Excess water was removed by sublimation and  $\text{cis-[Cr(NH}_3)_2(\text{OH}_2)_2\text{-Cl}_2]^+$  which is the only monopositive chromium(III) species in the reaction product was obtained free of other chromium species by cation exchange chromatography as described at method B. 0.2 M  $\text{NaClO}_4$ -solution at pH  $\sim$  2 was used as eluent. Production and purification of *cis*-diamminetetraaqua chromium(III) from this eluate followed closely method B, *i.e.* reaction with Hg(II) followed by cation exchange chromatography.

In most C-type experiments attempts were made to accelerate the water exchange using  $\text{CO}_2/\text{HCO}_3^-$  which is known to be an effective catalyst for oxygen exchange in the pentaammineaqua chromium(III) ion.<sup>5</sup> The amount of oxygen-18 introduced was, however, not reproducible (experiments C1

and C3–C6 in Table 1), and was also significantly smaller than that of the uncatalyzed reaction (experiment C2 in Table 1).

All manipulations of oxygen-18 enriched complexes including the ion exchange separations were carried out in the dark and at temperatures below 5  $^\circ\text{C}$  in order to minimize water exchange prior to the kinetic runs. *cis*-Diamminetetraaqua chromium(III) prepared by all three methods had spectral characteristics in complete agreement with those of this cation prepared by other methods.<sup>6</sup>

*Kinetic measurements, methods of analyses, spectrophotometric measurements and mass spectrometric measurements* were performed essentially as described previously.<sup>1</sup>

*Method of calculation.* The measured  $\delta$ -values were corrected for isotope fractionation during sublimation by the empirical function earlier established.<sup>1</sup> The corrected  $\delta$ -values as function of time,  $\delta_{\text{corr},t}$ , were approximated by a curve calculated from:

$$\delta_t = \delta_0 + \delta_1 [1 - \exp(-k_1 t)] + \delta_2 [1 - \exp(-k_2 t)]$$

with the two rate constants  $k_1$  and  $k_2$  and the three measures of oxygen-18 concentrations  $\delta_0$ ,  $\delta_1$  and  $\delta_2$ , *cf.* Appendix and Ref. 1, estimated by minimization of:

$$\sum_t (\delta_{\text{corr},t} - \delta_t)^2 / \sigma^2(\delta_{\text{corr},t})$$

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 experimental data are shown in Fig. 2. The further calculations to yield activation parameters were carried out as described previously.<sup>7</sup> It should be noted that the mathematical form of eqn. (1), with  $k_1$  not very

Table 1. Summary of kinetic data for water exchange in  $cis\text{-}[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$  in 0.50 M  $\text{HClO}_4$  + 0.50 M  $\text{NaClO}_4$ .

Exp. <sup>a</sup>	Temp. [°C]	[Cr(III)] [mM]	$\delta'_1$ [ <sup>18</sup> O/Cr]	$\delta'_2$ [ <sup>18</sup> O/Cr]	$\delta'_1 + \delta'_2$ [ <sup>18</sup> O/Cr]
A1	15.1	1.52	$1.48 \pm 0.24$	$1.34 \pm 0.19$	$2.82 \pm 0.06$
A2	24.9	1.04	$1.49 \pm 0.14$	$1.81 \pm 0.13$	$3.30 \pm 0.04$
A3	35.1	1.20	$1.31 \pm 0.15$	$1.73 \pm 0.14$	$3.04 \pm 0.04$
B1	25.2	2.22	$0.53 \pm 0.06$	$0.76 \pm 0.05$	$1.29 \pm 0.03$
B2	25.2	1.84	$0.50 \pm 0.07$	$0.76 \pm 0.05$	$1.26 \pm 0.03$
C1	15.2	2.39	$0.38 \pm 0.06$	$0.25 \pm 0.05$	$0.66 \pm 0.02$
C2	25.0	1.80	$0.84 \pm 0.06$	$0.36 \pm 0.06$	$1.20 \pm 0.02$
C3	25.2	2.29	$0.47 \pm 0.06$	$0.22 \pm 0.09$	$0.69 \pm 0.04$
C4	25.2	1.61	$0.41 \pm 0.05$	$0.10 \pm 0.05$	$0.51 \pm 0.02$
C5	25.2	2.38	$0.39 \pm 0.04$	$0.10 \pm 0.04$	$0.49 \pm 0.02$
C6	35.1	3.05	$0.50 \pm 0.04$	$0.27 \pm 0.04$	$0.77 \pm 0.01$

$k_1$  (25 °C)  $\sim (4.94 \pm 0.37) \times 10^{-5} \text{ s}^{-1}$ ;  $\Delta H_1^* \sim 100.9 \pm 2.8 \text{ kJ mol}^{-1}$ ;  $\Delta S_1^* \sim +11 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $k_2$  (25 °C)  $\sim (1.024 \pm 0.087) \times 10^{-5} \text{ s}^{-1}$ ;  $\Delta H_2^* \sim 105.3 \pm 4.2 \text{ kJ mol}^{-1}$ ;  $\Delta S_2^* \sim +13 \pm 14 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $\rho(k_1, k_2)^b \sim 0.741$ ;  $\rho(\Delta H_1^*, \Delta H_2^*)^b \sim 0.873$

<sup>a</sup> Prefixes A, B and C refer to the method of preparation of  $cis\text{-}[\text{Cr}(\text{NH}_3)_2(\text{OH}_2)_4]^{3+}$  as described in the experimental section. <sup>b</sup> Correlation coefficients.

different from  $k_2$ , seriously limits the accuracy of the kinetic parameters for this system compared to systems in which only *one* exchange process takes place. Therefore the uncertainties of rate constants and activation energies for the *cis*-diamminetetraaquachromium(III) ion are significantly larger, but strongly positively correlated, *cf.* the correlation coefficients,  $\rho$ , of Table 1, than those earlier determined by us, using the same experimental approach, for aqua complexes with only one type of water ligands present.

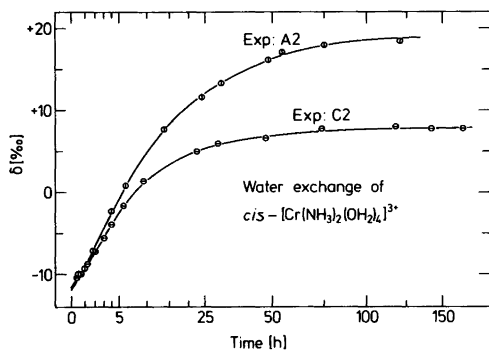


Fig. 2. Reaction kinetic experiments for water exchange in *cis*-diamminetetraaquachromium(III). The solid curves have been calculated from the parameters of Table 1.

## RESULTS AND DISCUSSION

Exchange of oxygen-18 labelled water from *cis*-diamminetetraaquachromium(III) equilibrated in this solvent takes place with retention of the ammine configuration. The exchange follows a sum of two exponential functions and this is illustrated by exp. A2 in Fig. 2. Two rate constants can be determined from such an experiment, and as they differ by only a factor of about 5, *cf.* Table 1, the kinetic parameters cannot be very accurately determined, *cf.* the experimental section. From the experiments A1, A2 and A3 of Table 1 it seems, however, that the preexponential factor to the term containing the larger rate constant, *i.e.*  $\delta'_1$ , is smaller than  $\delta'_2$  and an average ratio  $\delta'_1/\delta'_2 \sim 0.82 \pm 0.09$  is obtained from these three experiments. If the water exchange takes place with retention of configuration of not only the ammonia ligands which is observed experimentally but also of the unsubstituted water ligands,  $\delta'_1 = \kappa_N$  and  $\delta'_2 = \kappa_O$ , *cf.* Appendix, and  $\delta'_1/\delta'_2 = 1$  should therefore be expected for these experiments. A value smaller than 1 could point towards a larger extent of exchange during the purification steps of the 'fast' water ligand site than of the 'slow' site, but it could also be that the smaller ratio is the result of a non-stereoretentive water exchange reaction of the type

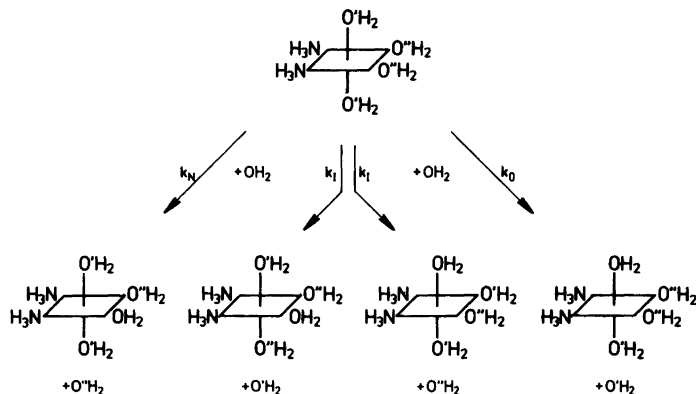


Fig. 3. Water exchange in *cis*-diamminetetraaquachromium(III) by stereoretentive processes,  $k_N$  and  $k_0$ , and by processes accompanied by isomerization,  $k_1$ .

labelled with  $k_1$  in Fig. 3. The mathematics of this latter suggestion is analyzed in Appendix, and will give  $\delta$ -ratios smaller than 1.\*

To differentiate between the two possibilities outlined above it was attempted to label the *cis*-diamminetetraaquachromium(III) ion stereospecifically with oxygen-18 by induced silver(I) or mercury(II) aquations as schematically outlined in Fig. 1. Such induced aquations normally proceed with retention of configuration, and this observation was the basis for the two attempted preparative routes B and C in Fig. 1.

Silver(I) accelerated removal of the chloride ligands in oxygen-18 enriched water, from a complex with the water ligands *trans* to the ammonia ligands of normal isotopic distribution, was first tried. This method, B, however, turned out to be

\* Three types of *trans* attack reactions have not been included in Fig. 3.

One of these is the reaction which isomerizes the *cis*-diammine to the *trans*-diammine. This reaction is not observed experimentally but at 70 °C it is estimated to have a rate constant which is smaller than  $0.06 \times 10^{-5} \text{ s}^{-1}$ .<sup>6</sup>

The other reaction shifts one of the water ligands between the two equivalent positions *trans* to ammonia simultaneously with exchange of the other water ligand of this type. Contributions from such a process will therefore be described by the  $k_N$ -path.

Finally the third reaction type is that which moves an ammonia ligand but maintains the *cis*-diammine configuration. It can be shown that contributions from this type of process will be described by both the  $k_0$  and  $k_1$  rate constants. Ammine isomerization processes are, however, at least a thousandfold slower than the present water exchange reactions, and contributions from this latter type of process are therefore very unlikely.

less successful as the rate of water exchange in the chloride ligand containing species was apparently fast enough to label significant amounts of water ligands already present in the complex by solvent exchange. Thus, even if the accelerated chloride ligand removal was stopped at the formation of monochloridocomplex, the generated *cis*-diamminetetraqua-ion contained about 1.28 <sup>18</sup>O/Cr, which based on a 95 % oxygen-18 content of the reactant water, means that at least  $1.28 - 0.95 \sim 0.33$  <sup>18</sup>O/Cr are introduced by a solvent exchange path. It is significant, however, that the average  $\delta$ -ratio for this type of experiment:  $\delta'_1/\delta'_2 \sim 0.76 \pm 0.09$  is comparable to but slightly smaller than that observed for the kinetic experiments based upon *cis*-diammine ion labelled by method A.

The faster water exchange in the dichlorido ion of the starting material observed by the B-type experiments provided the basis for some more successful attempts to label the water ligands *trans* to the ammonia ligands by method C of Fig. 1. For this type of experiment  $\delta'_1$  was invariably found greater than  $\delta'_2$ , the average ratio being  $\delta'_1/\delta'_2 \sim 2.0 \pm 0.3$ .

The presence of two differently coordinated types of water ligands in *cis*-diamminetetraaquachromium(III) provides an opportunity, not present in complexes with only equivalently coordinated water ligands, to investigate the relative importance of *cis*,  $k_N$ - and  $k_0$ -paths of Fig. 3, *vs.* *trans* attack,  $k_1$ -paths of Fig. 3, of the entering water ligand by the water exchange reactions. Kinetic schemes composed of these types of reactions may be analyzed as shown in Appendix.

The variation in  $\delta'_1/\delta'_2$  ratios as function of the mode of preparation of the *cis*-diammine ion and the known configuration of the diamminediaquachloridochromium(III) ion of the starting material<sup>8</sup> unequivocally assigns the greater rate constant primarily to the reactivity of the water ligands *trans* to the ammonia ligands, the  $k_N$ -path.

Since  $k_N$ ,  $k_O$  and  $k_1$  are all positive or zero, eqn. Ap 1 and the experimental data in Table 1 limit  $k_1$  to values smaller than  $0.275 \times 10^{-5} \text{ s}^{-1}$  at 25 °C. For this range of  $k_1$ -values  $16k_1^2 \ll (k_N - k_O)^2$  and eqn. Ap 1 may be reduced to

$$k_1 \sim k_N + 4k_1 \quad (1)$$

$$k_2 \sim k_O + 4k_1$$

The validity of these approximations may be tested by noting that they give:

$$k_1 \lesssim (0.26 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$$

in good agreement with the maximum value of  $0.275 \times 10^{-5} \text{ s}^{-1}$  derived from the exact equations.

A more detailed analysis of the  $\delta'$ -values can further significantly reduce this value. Eqn. Ap. 2 in the Appendix may be reduced by applying eqn. 1 to give:

$$\kappa_N \sim \delta'_1 + \frac{2k_1(\delta'_1 + \delta'_2)}{k_1 - k_2}$$

and

$$\kappa_O \sim \delta'_2 - \frac{2k_1(\delta'_1 + \delta'_2)}{k_1 - k_2} \quad (2)$$

Solvent exchange prior to the kinetic run will most likely make  $\kappa_N$  smaller than  $\kappa_O$ . Assuming  $\kappa_N \lesssim \kappa_O$  allows the much more restrictive estimate on  $k_1$  at 25 °C:

$$k_1 \lesssim (0.09 \pm 0.04) \times 10^{-5} \text{ s}^{-1} \quad (3)$$

to be made using eqn. 2 and averaged  $\delta'$ -data for experiments A1, A2 and A3. In combination with eqn. 1 this allows estimation of  $k_N$  and  $k_O$  at 25 °C as:

$$(4.6 \pm 0.4) \times 10^{-5} \text{ s}^{-1} \lesssim k_N \lesssim (4.9 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$$

and

$$(0.66 \pm 0.18) \times 10^{-5} \text{ s}^{-1} \lesssim k_O \lesssim (1.02 \pm 0.09) \times 10^{-5} \text{ s}^{-1}$$

*i.e.* the exchange of both types of water ligands is largely stereoretentive in 0.5 M acid solution.

At higher pH-values the water exchange is less stereoretentive, and this may be demonstrated by analyzing the C-type experiments using the upper limit for  $k_1$  given by eqn. 3. For exp. C2 it may thus be calculated from eqns. 2 and 3:

$$0.84 \pm 0.06 \lesssim \kappa_N \lesssim 0.90 \pm 0.07$$

and

$$0.36 \pm 0.06 \gtrsim \kappa_O \gtrsim 0.30 \pm 0.07 \quad (4)$$

The non-zero value for  $\kappa_O$  is particularly significant as this means that some isomerization of the water ligands must have taken place prior to the kinetic runs. This isomerization may occur either at the generation of the ammineaqua ion from the dichlorido complex, or, more likely, during the process of purification either by reaction through a base-catalyzed path at pH ~ 2 where the separations are carried out or catalyzed by the ion exchange resin. In this context it is noteworthy that the prepared aqua ions contain less oxygen-18 than estimated on the basis of the purity of the reactant oxygen-18 water, and the rate constants for water exchange in more acid solution.  $k_1$  of Table 1 extrapolated to 0 °C, the temperature at which the separations are carried out, indicates  $t_{1/2} \sim 180 \text{ h}$  for this process, to be compared with the time for purification of less than 1 h. Therefore base catalysis does probably operate although resin accelerated reactions are also known to occur for some similar complex ions.<sup>9</sup>

The contribution from an isomerization process to the base- or resin-catalyzed reaction can also be seen to be significantly greater than that observed for the kinetic experiments in strongly acid solution. Thus if it is assumed that the mercury(II) treatment of the dichlorido-complex generates the *cis*-diamminetetraaquachromium(III) ion with  $\kappa_O \sim 0.00$  and  $\kappa_N \lesssim 1.90$ , the upper limit for  $k_1$ :  $k_1 \lesssim 0.09 \times 10^{-5} \text{ s}^{-1}$  will give  $\kappa_N \gtrsim 1.11$  and  $\kappa_O \lesssim 0.09$ , for exp. C2 with  $\kappa_N + \kappa_O = 1.20$ , to be compared with the estimated values in eqn. 4 above.

In conclusion the water exchange reactions of *cis*-diamminetetraaquachromium(III) proceeds mainly by the  $k_N$  and  $k_O$  paths, and although both these paths may contain contributions from a nonstereoretentive process the small value for  $k_1$  makes it likely that the well-established stereoretentivity of thermal aquations of chromium(III)

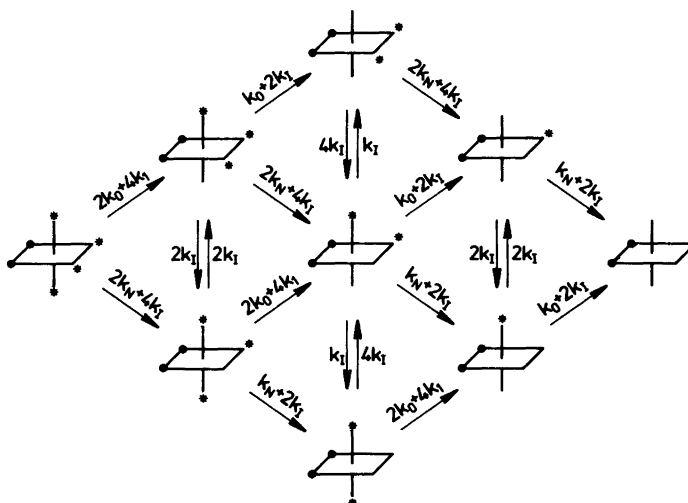


Fig. 4. Complete reaction scheme for irreversible oxygen-18 aquation in *cis*-diamminetetraaquachromium(III) by  $k_N$ ,  $k_O$  and  $k_I$  paths of Fig. 3. ● =  $\text{NH}_3$ ; \* =  $^{18}\text{OH}_2$ .

complexes is also observed for the present water exchange reactions in acid solution. However, significant water ligand isomerization does take place during the preparation of the *cis*-diamminetetraaquachromium(III) ion *via* a base- or ion exchange resin-catalyzed path.

A further discussion of the kinetic data reported here will be given when current investigations on the water exchange reactions of *mer*-triamminetriaqua- and amminepentaquachromium(III) have been concluded.

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## APPENDIX

The complete reaction scheme for water exchange in *cis*-diamminetetraaquachromium(III) by the elementary reactions shown in Fig. 3 is given in Fig. 4. This scheme has been analyzed in detail, and it can be shown that the concentration of oxygen-18 in the solvent,  $[^{18}\text{O}]$ , as function of time,  $t$ , is given by

$$[^{18}\text{O}] = [^{18}\text{O}]_{t=0} + [\text{Cr}] \times [\delta'_1(1 - \exp(-k_1t)) + \delta'_2(1 - \exp(-k_2t))]$$

with

$$(k_1, k_2) = \frac{1}{2}(k_N + k_O + 8k_I \pm \sqrt{(k_N - k_O)^2 + 16k_I^2}) \quad (\text{Ap. 1})$$

$$\delta'_1 = \frac{(k_O + 6k_I - k_1)(x_N(k_N + 4k_I - k_2) - 2x_O k_I)}{(k_N + 4k_I - k_2)(k_O + 4k_I - k_1) - 4k_I^2}$$

and (Ap. 2)

$$\delta'_2 = \frac{(k_N + 6k_I - k_2)(x_O(k_O + 4k_I - k_1) - 2x_N k_I)}{(k_N + 4k_I - k_2)(k_O + 4k_I - k_1) - 4k_I^2}$$

where  $x_N$  and  $x_O$  are the average number of oxygen-18 labelled water molecules *trans* to ammonia and water, respectively, at the start of the kinetic experiment.

## REFERENCES

1. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 34 (1980) 259 and references therein.
2. Moore, P., Basolo, F. and Pearson, R. G. *Inorg. Chem.* 5 (1966) 223.
3. Bracken, D. E. and Baldwin, H. W. *Inorg. Chem.* 13 (1974) 1325.
4. Andersen, P. and Berg, T. *To be published.*
5. Alexander, W. and Early, J. J. *Am. Chem. Soc.* 92 (1970) 2299.
6. Mønsted, L. and Mønsted, O. *Acta Chem. Scand.* 27 (1973) 2121.
7. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 32 (1978) 19.
8. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 32 (1978) 917.
9. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 28 (1974) 1040.

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