# Equilibration of Bromide with Pentaammineaquachromium(III) and the Mechanism of Substitution into Pentaammineaquachromium(III)

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A discrepancy of an order of magnitude has been reported in the overall equilibrium constant, K, for the reaction $[Cr(NH_3)_5(H_2O)]^{3+}+Br^- \rightleftharpoons [Cr(NH_3)_5Br]^{2+}+H_2O$, determined (a) by kinetic method (Ref. 1), and (b) equilibration studies (0.5 M Br^-) (Ref. 2). Although both values can be reproduced it is here argued that $K \sim 0.02$ M^{-1}, as determined by the latter method, is the true value at 25 °C, $I=1.00$ M (H,Na)(ClO$_4$,Br) $[Br^-] \rightarrow 0$. With inclusion of this value the free energy plot of log (k_{aq}/s^{-1}) vs. log (K/M^{-1}) for uninegative substituents gives a slope of 0.7. The mechanistic assignment for substitution into $[Cr(NH_3)_5(H_2O)]^{3+}$ remains borderline I_a/I_d.

The mechanism of substitution of pentaammineaquachromium(III):

$$[Cr(NH_3)_5(H_2O)]^{3+}+X^- \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} [Cr(NH_3)_5X]^{2+}+H_2O \qquad (1)$$
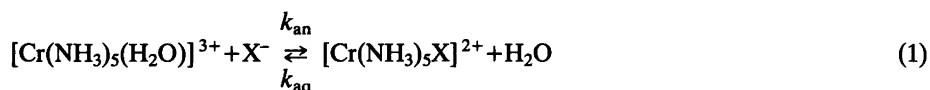
and whether this falls strictly within the definition of associative or dissociative interchange (I_a or I_d) has attracted much attention.[3] The now extensive experimental data point to the reaction being more dissociative than the corresponding reactions of $[Cr(H_2O)_6]^{3+}$, but whether the I_a or I_d description applies remains uncertain. In the linear-free-energy correlations used for both $[Cr(NH_3)_5(H_2O)]^{3+}$ and $[Cr(H_2O)_6]^{3+}$, the small size of the overall 1:1 equilibrium constant, $K=k_{an}/k_{aq}$, has often made accurate measurements difficult. The equilibration of Br^- with $[Cr(NH_3)_5(H_2O)]^{3+}$ is such a case, and our two laboratories have reported values of K differing by as much as an order of magnitude. The *kinetic method* described[1] has yielded a value of 0.30 ± 0.04 M^{-1} ($I=1.0$ M), whereas the *method of mixtures*[2] in which solutions of known (excess) Br^- and varying $[Cr(NH_3)_5Br]^{2+}/[Cr(NH_3)_5(H_2O)]^{3+}$ ratios were prepared, and those solutions with negligible initial variation in absorbance at 270 nm as a function of time were assumed to contain the pentaammine complexes in equilibrium concentrations, has yielded a value of 0.019 ± 0.002 M^{-1} ($I=0.82$ M). These different values have in turn raised doubts about the slope of the log (k_{aq}/s^{-1}) vs. log (K/M^{-1}) free-energy plot for single-charged negative substituents,[4] which is

believed to be diagnostic of an I_d or I_a process, depending on whether the slope tends to 1.0 or 0.5.[3]

We have reproduced the earlier data of the two different methods. However, it has been shown that medium and/or specific ion effects seriously influence the interpretation of the kinetic data, giving a too large formation constant for the 1:1 complex.

EXPERIMENTAL

Equilibration rate constants at 50 °C, I=1.0 M (LiClO$_4$), were determined as previously,[1] either starting from $[Cr(NH_3)_5(H_2O)]^{3+}$ or $[Cr(NH_3)_5Br]^{2+}$ or a mixture of both at various [Br$^-$]. Earlier results were reproduced with rate constants independent of starting complex, which is a clear indication that NH$_3$ loss is not relevant. The method of mixtures was similar to that previously described,[2] at 50 °C, with I adjusted to 1.0 M (LiClO$_4$). This procedure was also used for studies with Cl$^-$ as the incoming ligand. Reactant concentrations were $[Cr(NH_3)_5(H_2O)^{3+}]$=(5−6)×10^{-3} M, $[Cr(NH_3)_5Br^{2+}]$=(0.01−1.0)×10^{-3} M, $[Cr(NH_3)_5Cl^{2+}]$=(0.5−1.1)×10^{-3} M, [Br$^-$]=0.25−0.9 M, [Cl$^-$]=0.5 M, [H$^+$]=0.1−0.5 M. The wavelengths used for the Br$^-$ and Cl$^-$ studies were 270 and 530 nm, respectively. Spectrophotometric changes were monitored at the appropriate wavelength on Unicam SP500 Series II and Cary 219 instruments, fitted with a thermostatted cell holder and using stoppered quartz cells. First-order plots were linear to four half-lives. Concentrations of Br$^-$ and Cl$^-$ were estimated by titrimetric procedures involving either Ag(I) or Hg(II). Total Cr concentrations were determined by atomic absorption.

RESULTS AND DISCUSSION

Earlier kinetic results[1] (see also comments in Refs. 4 and 5) have been reproduced for Br$^-$. Determination of the slope/intercept for the appropriate plot at [Br$^-$]→0 gives K=0.30±0.04 M^{-1} as previously reported. The method of mixtures gives K: 0.016±0.002 M^{-1} at [Br$^-$]=0.9 M, 0.021±0.002 M^{-1} at [Br$^-$]=0.50 M and 0.021±0.003 M^{-1} at [Br$^-$]=0.25 M. Linear extrapolation gives a value of 0.025±0.005 M^{-1} for [Br$^-$]→0 M. Different values obtained by the two methods are not therefore due to inaccuracies in individual determinations.

For reactions in which a 2+ reactant is proceeding to a 3+ product (or vice versa) exchange of ClO$_4^-$ by Br$^-$ can understandably give rise to medium effects. The effect of changing one salt for another at constant ionic strength on rate or equilibrium constants can frequently be expressed by:[6]

$$k \approx k° (1+\alpha[X^-])$$

where α_X is a proportionality constant indicating the extent of the medium effect. In kinetic experiments on reactions of the type (1), the rate constant k_{eq} for equilibration in the absence of médium effects, is given by:

$$k_{eq}=k_{aq}+k_{an}[X^-]=k_{aq}(1+K[X^-]) \tag{2}$$

Allowing for medium effects upon k_{aq} and k_{an}, i.e.:

$$k_{aq}=k_{aq}°(1+\alpha_{aq}[X^-]) \quad \text{and} \quad k_{an}=k_{an}°(1+\alpha_{an}[X^-])$$

eqn. (2) is transformed into:

$$k_{eq}=k_{aq}^o+(k_{aq}^o\alpha_{aq}+k_{an}^o)[X^-]+k_{an}^o\alpha_{an}[X^-]^2\approx k_{aq}^o\,(1+(K+\alpha_{aq})[X^-]) \tag{3}$$

Comparison of eqs. 2 and 3 clearly identifies the kinetically determined equilibrium constants, K_{kin}, as the sum of the true equilibrium constant, $K=k_{an}^o/k_{aq}^o$, and the parameter for the medium effect on the aquation rate constant, i.e.
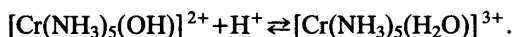
$$K_{kin}\approx K+\alpha_{aq} \tag{4}$$

For the present system, with $K_{kin}\approx0.30\pm0.04$ M^{-1} and $K\approx0.025\pm0.005$ M^{-1}, $\alpha_{aq}\approx$ $+0.28\pm0.05$ M^{-1} is obtained. This value of α_{aq}, different from zero, is the result of differences in ionic interactions between the negatively charged perchlorate and bromide ions, and the positively charged ground state and transition state. The sign of α_{aq} and the generally known tendency of bromide ions to form stronger outer sphere complexes than perchlorate ions, is indicative of greater stabilization of the transition state than of the ground state by ion-pair formation with bromide ions, and this could be caused by partial dissociation of the anionic leaving ligand in the transition state, giving this an effectively higher charge.

This interpretation is supported by the variation of some equilibrium constants between doubly and triply charged cations in 1.00 M Na(Br, ClO$_4$), which shows a relative stabilization of the higher charged cation with increasing bromide concentration. The trend is seen in the equilibrium data by the method of mixtures for

$$[Cr(NH_3)_5Br]^{2+}\rightleftarrows[Cr(NH_3)_5(H_2O)]^{3+}+Br^-$$
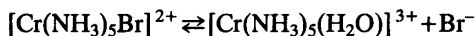
and has been accurately measured[9] for

$$[Cr(NH_3)_5(OH)]^{2+}+H^+\rightleftarrows[Cr(NH_3)_5(H_2O)]^{3+}.$$

The acid dissociation constant of the pentaammineaquachromium(III) ion in the latter process can be described by

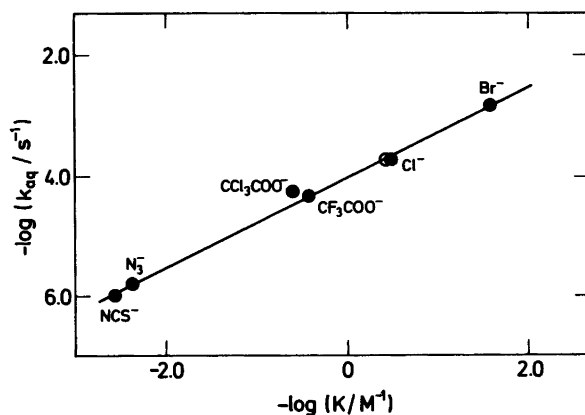
Fig. 1. Linear free-energy plot of log (k_{aq}/s^{-1}) against $-\log$ (K/M^{-1}) for acidopentaamminechromium(III) complexes at 50 °C, I=1.00 M (LiClO$_4$ or NaClO$_4$). See also the text.

$$K_a^{-1} \approx K^\circ(1 + a[\text{Br}^-])$$

with $K^\circ \approx 10^{5.180 \pm 0.011}$ M^{-1} and $a \approx 0.18 \pm 0.05$ M^{-1} in agreement with the sign and in qualitative agreement with the order of magnitude of a_{aq}. The lower equilibrium constant, K, obtained by the method of mixtures is therefore the true value, and this point is that shown in Fig. 1. It is noted that with all other anions in Fig. 1 the bigger K values, cf. eqn. (4), serve to make the kinetically determined K much less influenced by medium effects. Thus for Cl^- the kinetic method[1] gives $K \approx 0.40 \pm 0.02$ M^{-1}, whereas at $[\text{Cl}^-] = 0.5$ M in 1.00 M $(\text{H,Na})(\text{Cl,ClO}_4)$ $K \approx 0.31 \pm 0.02$ M^{-1} is obtained by the method of mixtures. The difference between these two values, both shown in Fig. 1, can hardly be seen.

A slope of 0.70 ± 0.02 is now obtained for the free energy plot in Fig. 1. As previously indicated, the spread of anation rate constants, k_{an}, is >10,[4] which might be said to favour an I_a assignment. However, a case for an I_d assignment can also be made,[5] which makes the application of the I_a/I_d nomenclature less useful. It is interesting to note that the volume of activation $\Delta V^{\neq}$ of -5.8 cm^3 mol^{-1} for H_2O exchange on $[\text{Cr(NH}_3)_5(\text{H}_2\text{O})]^{3+}$ is midway between the extremes noted for other oxidation state (III) metal ions, which range from $+1.2$ cm^3 mol^{-1} for $[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{3+}$, an I_d process, to -9.3 cm^3 mol^{-1} for $[\text{Cr(H}_2\text{O})_6]^{3+}$ and -10.1 cm^3 mol^{-1} for $[\text{V(H}_2\text{O})_6]^{3+}$, which are believed to be I_a.[7,8] In fact, a linear correlation between volumes of activation for water exchange and slopes in linear free-energy plots of the type shown in Fig. 1 has been demonstrated for several series of metal complexes.[2] Both volumes of activation and linear free-energy relations suggest that substitution reactions in the pentaamminechromium(III) series of complexes are *less* associative than reactions in the pentaaquachromium(III) series, and *more* associative than reactions in the pentaammine-rhodium(III), -iridium(III), and -cobalt(III) series.[2]

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