Outer-sphere Complexes of $Cr(NH_3)_5X^{2+}$ with Benzenehexacarboxylate Anion

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Summary A kinetic and potentiometric study of the outer-sphere complexes formed in aqueous solution between benzenehexacarboxylate anions and halogenopenta-amminechromium(III) cations, suggests the formation of 1 : 1, 1 : 2, and 1 : 3 ion-pair species.

ANIONS including polycharged carboxylates have been shown to form 1 : 1 ion-pairs or outer-sphere complexes with both chromium(III) and cobalt(III) halogenopenta-ammine complexes.[1,2] The stability constants for some of these systems have been calculated both from kinetic and potentiometric data.[2,3] Outer-sphere complex formation between bromopenta-ammine anions such as pyrophosphate and hexacarboxylate result in an increase in the observed rate of aquation, as shown in Figure 1. The increase in rate can be attributed to the faster aquation of the outer-sphere complex.

$$\begin{tikzcd} Cr(NH_3)_5X^{2+} + H_2O \arrow[r, "k_1"] \arrow[d, shift right, "K_{\text{assoc}}"'] & Cr(NH_3)_5H_2O^{3+} + X^- \\ Cr(NH_3)_5X \cdots\cdots A^{n-2} \arrow[u, shift right, "+\ \text{Anion}\ (A^{n-})"'] \arrow[r] & Cr(NH_3)_5H_2O \cdots A^{n-3} + X^- \end{tikzcd}$$

(outer-sphere complex)

$$K_{\text{assoc}} = \frac{[Cr(NH_3)_5X \cdots\cdots A^{n-3}]}{[Cr(NH_3)_5X^{2+}][A^{n-}]} \qquad (1)$$

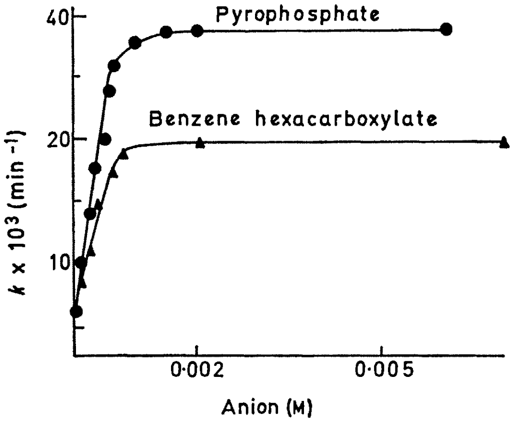

FIGURE 1. *Effect of sodium pyrophosphate and sodium hexacarboxylate on the rate of aquation of bromopenta-amminechromium-*(III) *perchlorate at* 25°.

The observed rate, obtained by following the disappearance of $Cr(NH_3)_5X^{2+}$ species, either by a polarographic or spectrophotometric technique can be expressed:

$$k_{\text{obs(complex)}} = k_1[Cr(NH_3)_5X^{2+}] + k_2[Cr(NH_3)_5X \cdots\cdots A^{n-2}] \qquad (2)$$

Substituting from Equation 1:

$$k_{obs} = \frac{k_1 + k_2KA}{1 + KA} \qquad (3)$$

k_2 is the limiting rate constant at high anion concentration when all the complex is in the outer-sphere form. Thus, K, the association constant, can be calculated from the kinetic data.

When the added salt is sodium benzenehexacarboxylate the kinetic expression in Equation 2 can only be evaluated by assuming the formation of 1 : 1, 1 : 2, and 1 : 3 outer-sphere complexes, between the anion and complex. From Figure 1 it can be seen that the observed rate is doubled when the concentration of added hexacarboxylate anion is less than 2×10^{-4}M, the concentration of the complex being 5×10^{-4}M. From the kinetic data, it is however, only possible to calculate the overall stability constant $\log\beta_3$ ($9{\cdot}88 \pm 0{\cdot}13$) over the anion range $0{\cdot}59$—$1{\cdot}75 \times 10^{-4}$M. From independent potentiometric studies of the stability of the outer-sphere complexes under similar conditions it has been possible to evaluate the stepwise stability constants $\log K_1 = 4{\cdot}3$ ($\pm 0{\cdot}3$), $\log K_2 = 4{\cdot}1$ ($\pm 0{\cdot}2$), $\log K_3 = 3{\cdot}1$ ($\pm 0{\cdot}3$).

The suggested structure of the 1 : 3 outer-sphere complex is believed to involve hydrogen bonding between the carboxylate group and the ammine hydrogen in the inner sphere of co-ordination as shown in Figure 2.

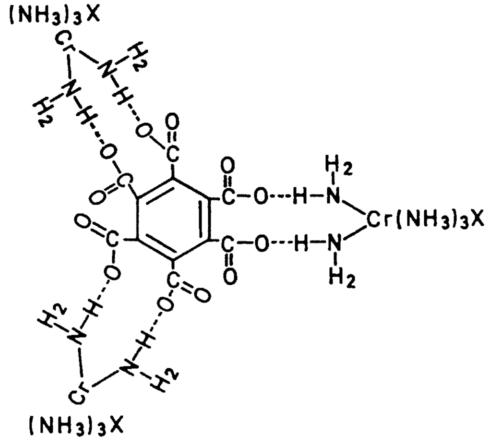

FIGURE 2. *Suggested structure for* 1 : 3 *hexacarboxylate–bromopenta-amminechromium*(III) *outer-sphere complex.*

From aqueous acetone solutions a crystalline salt giving analysis in reasonable agreement with a 1 : 3 stoicheiometry has been isolated.

(*Received, April* 10*th*, 1970; *Com.* 512.)

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[3] S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, **1965**, 724.