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Mechanistic Studies on the Reaction of Pentaaquahydroxochromium(III) Ion with Oxalic Acid†

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The substitution of aqua ligands from pentaaquahydroxochromium(III) ion by oxalic acid occurs through a mechanism involving the formation of an ion pair followed by an associative interchange (I_a) process.

Previous studies[1–6] have shown that the anation reactions of $[Cr(H_2O)_5(OH)]^{2+}$ with incoming ligands containing N,O donor centres occur through an associative interchange (I_a) mechanism, while those with ligands containing N,N donor centres proceed through a dissociative mechanism. To our knowledge, the mechanism of the anation of $[Cr(H_2O)_5(OH)]^{2+}$ by ligands containing O,O donor centres has not been studied, though the reactions of $[Cr(H_2O)_6]^{3+}$ with oxalate ions have been reported previously.[7,8] Compared with $[Cr(H_2O)_6]^{3+}$, the co-ordinated OH in $[Cr(H_2O)_5(OH)]^{2+}$ facilitates a dissociative mechanism through its π-bonding ability, but it seems that the ligand donor power has an important influence on mechanism. The present investigation is concerned with the mechanism of anation of $[Cr(H_2O)_5(OH)]^{2+}$ by a ligand containing a O,O donor centre (oxalic acid) and the influence of the ligand donor power.

Experimental

Hexaaquachromium(III) perchlorate was prepared by the literature method.[9] Pentaaquahydroxochromium(III) was prepared *in situ* by adjusting the pH of a solution of $[Cr(H_2O)_6]^{3+}$ to 5.0 {the percentage of $[Cr(H_2O)_5(OH)]^{2+}$ is estimated to be 85% at 25 °C and pH 5.0 from the acid dissociation constants[10]} and was verified from the absorption spectrum, λ_{max} at 430 ($\log \epsilon = 1.422$) and 590 nm ($\log \epsilon = 1.121$). All the chemicals used were of AR grade. The composition of the product in solution was determined by changing the molar ratios of the two reactants and by Job's method of continuous variation. The metal to ligand ratio was found to be 1:1. The reaction course was monitored with a UV-265 spectrophotometer (Shimadzu, Japan) at 315 nm where the molar absorption coefficients of the reactant complex and product differ appreciably. The pH was adjusted by $NaOH/HClO_4$ using a pHS-3 digital pH meter, and the ionic strength of the reaction medium by adding $NaClO_4$. The [ligand] was always maintained high so that a pseudo-first-order rate law would be obeyed. All data were treated by a least-squares procedure.

Results and Discussion

At fixed [ligand] (0.1 mol dm^{-3}), pH 5.0, ionic strength I (0.2 mol dm^{-3}) and at different $[Cr(H_2O)_5(OH)]^{2+}$ concentrations (0.005, 0.00625, 0.0075 mol dm^{-3}), the k_{obs} values are 3.49×10^{-4}, 3.41×10^{-4} and 3.32×10^{-4} s^{-1} respectively at 35 °C. Thus the rate of reaction showed a first-order dependence on $[Cr(H_2O)_5(OH)^{2+}]$.

Table 1 Influence of pH on k_{obs} (308 K)[a]

pH	4.4	4.6	4.8	5.0	5.2
$10^4\ k_{obs}$/s^{-1}	1.75	1.80	2.03	3.49	4.40

[a] $[Cr(H_2O)_5(OH)^{2+}] = 0.005$ mol dm^{-3}, [ligand] = 0.10 mol dm^{-3}, $I = 0.2$ mol dm^{-3}.

The rate of reaction was found to increase with increasing pH of the medium (Table 1). This can be explained by considering the pK values of the incoming ligand and the reactant complex. According to the following equilibria

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- \rightleftharpoons C_2O_4^{2-}$$
$$(pK_1 = 1.27, pK_2 = 4.27 \text{ at } 25\ °C)$$

it is obvious that the percentage of the dinegative anionic form $C_2O_4^{2-}$, which can be calculated to be 84% at 25 °C and pH 5.0 by using the pK_1 and pK_2 values, will increase with the increase in pH and it has a higher donor power. Thus, the rate of reaction increases with pH. Considering the acid dissociation equilibrium

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H^+$$
$$(pK = 4.0 \text{ at } 25\ °C)$$

the percentage of the more reactive pentaaquahydroxo species increases with increasing pH. The enhanced reactivity of this species is due to the well known labilising effect of the hydroxide ion adjacent to the water molecule through its lone pair of electrons exerting a strong electromeric effect. Hydroxide ion is also a strong π donor which facilitates the formation of very reactive hydroxo intermediates and thus inceases the rate.

The results of the variation of [ligand] on the reaction rate at 27, 30, 35, 38 and 40 °C are illustrated in Fig. 1. The rate of reaction increases with increase in [ligand] and at high [ligand] approaches a limiting value due to completion of ion-pair formation.[11] The following mechanism is proposed to explain the variation of rate with [ligand].

$$[Cr(H_2O)_5(OH)]^{2+} + C_2O_4^{2-} \overset{K_E}{\rightleftharpoons} [Cr(H_2O)_5(OH)]^{2+}\bullet C_2O_4^{2-} \tag{1}$$

$$[Cr(H_2O)_5(OH)]^{2+}\bullet C_2O_4^{2-} \xrightarrow[\text{slow}]{k_a} [Cr(H_2O)_3(OH)(C_2O_4)] + 2H_2O \tag{2}$$

Based on reactions (1) and (2) and considering the ion-pair equilibrium and rate-determining step, the following rate law can be derived:

$$\frac{d[Cr(H_2O)_3(OH)(C_2O_4)]}{dt} = \frac{k_a K_E [Cr(H_2O)_5(OH)^{2+}]_T [C_2O_4^{2-}]}{1 + K_E[C_2O_4^{2-}]}$$
$$= k_{obs}[Cr(H_2O)_5(OH)^{2+}]_T \tag{3}$$

where K_E is the ion-pair equilibrium constant, k_a the anation rate constant and $[Cr(H_2O)_5(OH)^{2+}]_T$ represents

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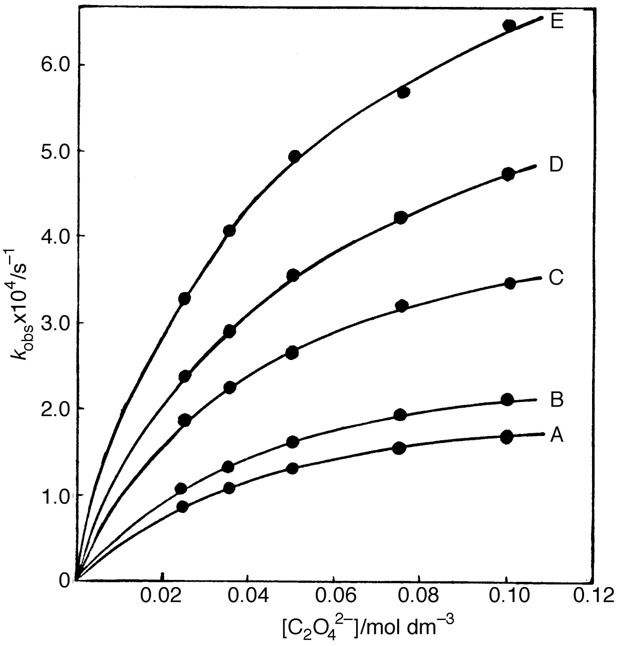

Fig. 1 Variation of k_{obs} with $[C_2O_4{}^{2-}]$ at different temperatures. (A) 27, (B) 30, (C) 35, (D) 38 and (E) 40 °C; $[Cr(H_2O)_5(OH)^{2+}] = 0.005\,mol\,dm^{-3}$, pH 5.0, $I = 0.2\,mol\,dm^{-3}$

the total unreacted complex concentration in solution. So,

$$k_{obs} = \frac{k_a K_E[C_2O_4{}^{2-}]}{1 + K_E[C_2O_4{}^{2-}]} \tag{4}$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{1}{k_a K_E[C_2O_4{}^{2-}]} \tag{5}$$

eqn. (5) suggests that plots of $1/k_{obs}$ *versus* $1/[C_2O_4{}^{2-}]$ at a constant pH should be linear with an intercept = $1/k_a$ and slope = $1/k_aK_E$, and this is indeed evidenced in Fig. 2. The k_a values are 2.37×10^{-4}, 3.10×10^{-4}, 4.83×10^{-4}, 6.98×10^{-4} and 8.91×10^{-4} s^{-1} at 27, 30, 35, 38 and 40 °C respectively, The K_E values are found to be 21 to 26 dm^3 mol^{-1} in the temperature range studied.

Activation parameters were calculated from the linear Eyring plot of log k_a/T *versus* $1/T$ and the values of $\Delta H^‡$ and $\Delta S^‡$ found to be 76.2 kJ mol^{-1} and –60.7 J K^{-1} mol^{-1} respectively. The high ion-pair equilibrium constant indicates the interaction between a bipositive cation $[Cr(H_2O)_5(OH)]^{2+}$ and a binegative anion $C_2O_4{}^{2-}$. Compared to the rate of isotopic water exchange, the high anation rate constant suggests the associative character of the interchange process, *i.e.* bond formation by the incoming ligand plays a significant role in the interchange step, which is evidenced by the low value of $\Delta H^‡$. Moreover, the considerably negative $\Delta S^‡$ suggests the activated complex formation through outer-sphere association is stabilised by hydrogen bonding between a water molecule of the inner-sphere complex and the negative end of the oxalate ion, which leads to the formation of a stable and compact activated state. Based on the above discussion, we propose that the reaction occurs through an associative interchange (I_a) process. This is consistent with the anation of $[Cr(H_2O)_5(OH)]^{2+}$ by ligands containing N,O donor centres.[1–5] The complex $[Cr(H_2O)_5(OH)]^{2+}$ and the incoming ligands (N,O or O,O) form an ion-pair first. In the following slow step the O^- in the ligands replace the co-ordinated water molecule. The ion pair is stabilised by hydrogen bonding and the interaction between two reactants having opposite charges. We note however that the anation of $[Cr(H_2O)_5(OH)]^{2+}$ by ligands containing N,N donor centres occurs through a dissociative mechanism.[6] Compared with O^-,N has a weaker donor power and the incoming ligands are neutral molecules. It is difficult to form an ion pair between a complex ion and a neutral molecule containing N,N centres which has a lower donor power. Moreover, due to the σ- and π-bonding abilities of the hydroxo-group in $[Cr(H_2O)_5(OH)]^{2+}$, the OH group labilises the aqua ligand, producing a stable five-co-ordinate intermediate rather than an ion pair between two reactants. This leads to the conclusion that the nature of the incoming ligands has an important effect on the mechanism of the anation of $[Cr(H_2O)_5(OH)]^{2+}$, although the co-ordinated OH facilitates a dissociative mechanism. The increase in donor power of the incoming ligands is favorable to the I_a mechanism.

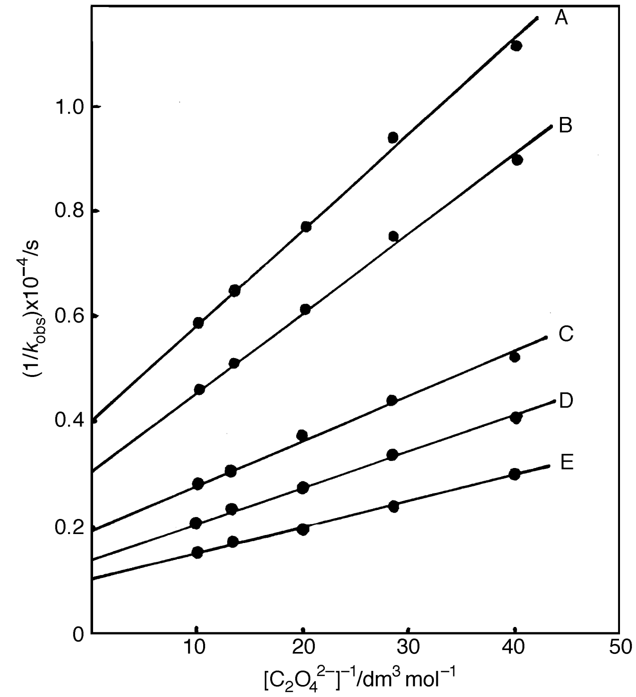

Fig. 2 Plots of $1/k_{obs}$ *versus* $1/[C_2O_4{}^{2-}]$ at different temperatures: (A) 27, (B) 30, (C) 35, (D) 38 and (E) 40 °C

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