Successive Complexation Steps in the Co-ordination Kinetics of the Dysprosium(III)–Acetate System

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Summary By controlling the ratio of metal ion to ligand concentrations in the Dy^{III}–acetate system, the complexation rate constant for the formation of the bisacetato-complex was found to be significantly larger than for the monoacetato-complex.

A PROBLEM of general interest in co-ordination chemistry is that of the effect of prior complexation upon the kinetics of successive complexation steps. The reaction between Dy^{III} and acetate was chosen as a model system because previous kinetic studies indicated that acetate complexation was unique among lanthanoid complexation reactions. Using jump techniques in the temperature range 6·5—25°, Dy^{III} complexation rate constants were approximately $1 \times 10^{7} M^{-1} s^{-1}$ with murexide,[1] anthranilate,[2] and oxalate,[3] while at 12·5° a rate constant equal to $9 \cdot 2 \times 10^{7} M^{-1} s^{-1}$ was reported for acetate,[4] with the suggestion that the acetate result corresponds to the formation of the bis complex. The measured rate constant was greater than the calculated Dy^{III}–water exchange rate of $6 \cdot 3 \times 10^{7} s^{-1}$,[5] a result which is inconsistent with the suggested mechanism of lanthanoid complexation in which cation–solvent exchange is a more rapid process than cation–ligand bond formation.[6] An alternative suggestion that the anomalous acetate results were caused by acetate acting as a multidentate ligand was in an ultrasonic relaxation study.[7] In that study the acetate concentration was maintained at three times that of the lanthanoid ion. The present study was carried out to see if the controlled introduction of bisacetato-complexation would eliminate the discrepencies in the literature.

The kinetic measurements were carried out on a temperature jump instrument (Messanlagen Studiengesellschaft m.b.h.) thermostatted with a Landa TK 30 DH bath. In the first series of experiments, Dy^{3+}, ClO_4^-, and NaOAc† were mixed so that the ratio of Dy^{III} to total acetate was at least ten to one at a pH less than 5·5 in order to prevent the formation of the bis complex. For reaction (1) the relaxation time expression is[2,4] equation (2). The data are shown in the Figure. A reiterative process was employed starting with a Dy^{III}–acetate formation constant in the previously reported range of 47[8] (20°, 2M-$NaClO_4$) to 107[8] (20°, 0·1M-$NaClO_4$) and modifying $\theta(c)$ and the kinetic formation constant until a self-consistent result was obtained.

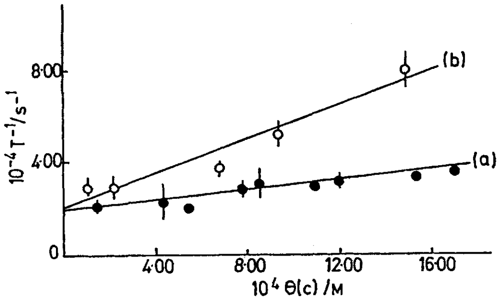

Figure. *Relaxation data:* (a) *cation–ligand ratio* ⩾ 10:1, (b) *cation–ligand ratio* ⩽0·5:1.

The results are $k_f = 1{\cdot}1 \times 10^7\ M^{-1}\,s^{-1}$, $k_b = 1{\cdot}9 \times 10^4\,s^{-1}$, and the calculated formation constant, $K_f = 570$ at 8·5°, in agreement with the kinetic data on other Dy^{III} systems.

In the second series of experiments the ratio of Dy^{III} to acetate was at least one to two. The Figure shows that an accelerated rate was observed under these conditions. The process must correspond to a coupled reaction in which the formation of the monoacetato- is slower than the formation of the bisacetato-complex. Using equations (2) and (3), which are not appropriate in this case, one would calculate

$$Dy^{3+} + OAc^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} DyOAc^{2+} \qquad (1)$$

$$\tau^{-1} = k_f\,\theta(c) + k_b \qquad (2)$$

where $\theta(c) =$

$$1 + \frac{([Dy^{3+})/[H^+]) + [OAc^-]}{K_a + [OAc^-]\{(K_{In} + [H^+]/(K_{In} + [H^+] + [In^-])\}} \qquad (3)$$

an overall rate constant of $3{\cdot}7 \times 10^7\ M^{-1}\,s^{-1}$, a reverse rate of $2{\cdot}1 \times 10^4\,s^{-1}$, and a coupled formation constant of $1{\cdot}8 \times 10^3$. This study involved only a limited pH range in which low concentrations of bis-complex were formed.

These experiments verify that the formation rate constant of $DyOAc^{2+}$ is similar to that of other Dy^{III} systems, as well as providing direct evidence for an increased formation rate of the bis over the monoacetato-complex. However, no information can be obtained from this study to decide if acetate acts as a bidentate ligand.

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† HOAc = acetic acid, HIn = protonated methyl red, and K_a and K_{In} are the dissociation constants of acetic acid and methyl red, respectively.

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