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Studies on kinetics of complexation of lanthanide α-hydroxycarboxylates with 1,10-phenanthroline

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Abstract—Kinetics of the coordination reaction of lanthanide (La^{III}, Eu^{III}) α-hydroxycarboxylates [$LnL_3(H_2O)_2$] with 1,10-phenanthroline (phen) in methanol–water (*v*/*v*, 3 : 2) were studied at 25°C by calorimetric titration. A one-step reaction process in accordance with the rate law has been suggested. The reaction is found to be first order for both lanthanide α-hydroxycarboxylates and phen. We have evaluated rate constants of the reactions. It is found that a linear free energy relationship exists between the stability constants of the lanthanide–α-hydroxycarboxylate–phen ternary complex and the rate constants. It is also found that a linear free energy relationship exists between the rate constants of La-hydroxycarboxylate with phen and the acid strength of α-hydroxy-acid as primary ligand, but the linear free energy relationship does not exist in the Eu–α-hydroxycarboxylate–phen ternary complex. The influence of other factors upon the reaction rate constants was also discussed. © 1997 Elsevier Science Ltd

Keywords: lanthanide α-hydroxycarboxylates; 1,10-phenanthroline; coordination reaction; rate constant; kinetics; linear free energy relationship.

α-Hydroxy-acids and their lanthanide complexes have been extensively investigated [1,2]. In our previous work [3,4] we have reported the thermodynamic properties of the complexation of La^{III}, Eu^{III} glycolate, La^{III}, Eu^{III} lactate, La^{III}, Eu^{III} mandelate and La^{III}, Eu^{III} atrolactate with phen in methanol–water (*v*/*v*, 3 : 2) at 25°C determined by calorimetric titration. We also studied the effect of substituent groups on the thermodynamic function of coordination of lanthanide α-hydroxycarboxylates with phen. In this paper, we discuss the chemical reaction kinetics of the reactions mentioned above.

EXPERIMENTAL

Reagents and apparatus

The reagents and the apparatus employed were the same as reported earlier [3,4].

Experimental procedure and calculation methods

The experimental procedure and the procedure used for calculating the concentration of species present in reaction vessel were similar to those described previously [3,4,5].

In continuous titration calorimetry, for the reaction

$$A+B = AB$$

where A represents titrant phen; B represents titrate $LnL_3(H_2O)_2$ [1]; AB represents the resultant LnL_3phen [3] (omitting resultant H_2O). Eleven data points at 11 min intervals are used in the calculation. In this experiment the total concentration of A ($[A_T]$) and the total concentration of B ($[B_T]$) in the reaction vessel are known, only the concentration of $[AB]_p$ is necessary to complete the calculation. The concentration of $[AB]_p$ was printed by using TP-801 computer (see Table 1).

At the experiment, the concentrations of phen (A) and $LnL_3(H_2O)_2$ (B) are almost the same, so we

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Table 1. The concentration of $La(C_6H_5CHOHCOO)_3$ phen ($[AB]_p$, given in mol dm^{-3}) present in reaction vessel of a 0.004793 mol dm^{-3} ($[A_T]$) phen solution with a 0.002743 mol dm^{-3} ($[B_T]$) $La(C_6H_5CHOHCOO)_3(H_2O)_2$ solution at 25°C in methanol–water (*v*/*v*, 3 : 2)

Time (min)	$[AB]_p$	$[A_T]-[AB]_p$	$[B_T]-[AB]_p$	$\mathrm{Log}\frac{[B_T]}{[A_T]}\frac{[A_T]-[AB]_p}{[B_T]-[AB]_p}$
1.00	0.0001908	0.0046022	0.0025522	0.014
2.00	0.0003641	0.0044289	0.0023789	0.028
3.00	0.0005209	0.0042721	0.0022221	0.042
4.00	0.0006624	0.0041306	0.0020806	0.055
5.00	0.0007898	0.0040032	0.0019532	0.069
6.00	0.0009044	0.0038886	0.0018386	0.083
7.00	0.0010073	0.0037857	0.0017357	0.096
8.00	0.0010998	0.0036932	0.0016432	0.109
9.00	0.0011828	0.0036102	0.0015602	0.122
10.00	0.0012575	0.0035355	0.0014855	0.134
11.00	0.0013246	0.0034684	0.0014184	0.146

assumed the rate equation of the reactions mentioned above can be expressed as

$$r = \mathrm{k}[\mathrm{phen}]^x[\mathrm{LnL}_3(\mathrm{H}_2\mathrm{O})_2]^y$$

where k is the rate constant of the reactions, L represents CH_2OHCOO^-, $CH_3CHOHCOO^-$, $C_6H_5CHOHCOO^-$, and $C_6H_5CH_3COHCOO^-$, respectively; Ln represents La^{III} or Eu^{III}. Assuming $x = y = 1$, plots of

$$\mathrm{Log}\frac{[B_T]}{[A_T]}\frac{[A_T]-[AB]_p}{[B_T]-[AB]_p}$$

against time (T) is a line and favour the assuming $x = y = 1$. In other words, the assumption is reasonable. It is proved that the reaction is found to be first order for both lanthanide α-hydroxycarboxylate and phen, and further proved that the rate equation of the reaction is $r = \mathrm{k}[\mathrm{phen}][\mathrm{LnL}_3(\mathrm{H}_2\mathrm{O})_2]$. The observed rate constants can be calculated from the slopes of the lines. The values of the observed rate constants of the reactions mentioned above are summarized in Table 2.

RESULTS AND DISCUSSION

As seen in Table 2, the values of the observed rate constants of the reactions are small, this is because the intermolecular hydrogen bond of $LnL_3(H_2O)_2$ with the solvent H_2O molecules is not favourable for the coordination of nitrogen atoms of phen. In the meantime, the space hindrance of phen due to its rigid structure is also not favourable for the coordination of phen.

As seen from Table 2, the order of the rate constants of the reaction with change in primary ligand is atrolactate > mandelate > lactate > glycolate for Eu^{III} or atrolactate > mandelate > glycolate > lactate for La^{III}. Log *k* values of the reactions appear to increase

Table 2. Observed rate constants and equilibrium constants [3] for complexation of several lanthanide α-hydroxycarboxylates with phen in methanol–water (*v*/*v*, 3 : 2) at 25°C

Complex	*k* (mol^{-1} dm^3 min^{-1})	Log *k*	Log *K*
$La(CH_2OHCOO)_3$phen	11.01 ± 0.02	1.04	2.18
$La(CH_3CHOHCOO)_3$phen	10.80 ± 0.02	1.03	2.17
$La(C_6H_5CHOHCOO)_3$phen	15.51 ± 0.01	1.19	2.44
$La(C_6H_5CH_3COHCOO)_3$phen	31.54 ± 0.02	1.50	2.78
$Eu(CH_2OHCOO)_3$phen	8.08 ± 0.03	0.91	2.04
$Eu(CH_3CHOHCOO)_3$phen	16.60 ± 0.01	1.22	2.41
$Eu(C_6H_5CHOHCOO)_3$phen	20.65 ± 0.03	1.32	2.51
$Eu(C_6H_5CH_3COHCOO)_3$phen	59.40 ± 0.04	1.77	2.99

Data are average values of three runs. The uncertainties are expressed as the standard deviation from the mean.

as the substituent groups of the α-hydroxy-acid increase and become large. This is because the intermolecular hydrogen bond of lanthanide α-hydroxycarboxylates $Ln(CH_2OHCOO)_3(H_2O)_2$, $Ln(CH_3CHOHCOO)_3(H_2O)_2$, $Ln(C_6H_5CHOHCOO)_3(H_2O)_2$ and $Ln(C_6H_5CH_3COHCOO)_3(H_2O)_2$ with the solvent H_2O molecules appears to decrease as the substituent groups of α-hydroxy-acid increase and become large and is favourable for the coordination of phen. The enhancement of the rate constants of the reaction in the order mentioned above was also explained by possible aromatic ring stacking (benzene ring of α-hydroxy-acid and phen ring). This definitely proves that the substituent effect does not play a predominant role amongst the factors that govern the coordination behaviour of the phen ligand.

On the basis of the above discussion, the reactions mentioned above are all one-step processes. The reaction process can be expressed as

$$LnL_3(H_2O)_2 + phen \xrightarrow{k} LnL_3phen + 2H_2O$$

The rate law in accordance with one-step reaction process is

$$\frac{d[LnL_3phen]}{dt} = k[LnL_3(H_2O)_2][phen]$$

which is in agreement with the previous assumption.

For a given α-hydroxycarboxylate and phen ligands the order of k is $La^{III} < Eu^{III}$ (except glycolate reaction systems). This is because the difference between the La^{III} and Eu^{III} character, which results from the solvation between $EuL_3(H_2O)_2$ and solvents being greater than that of $LaL_3(H_2O)_2$ and solvents and which give rise to the different k values.

For a given lanthanide and four different α-hydroxy-acid, it is found that a linear free energy relationship exists between the reaction rate constants (Log k) of $LnL_3(H_2O)_2$ with phen and the stability constants (Log K) of LnL_3phen (see Figs 1 and 2). The linear relationship between Log k and Log K indicate that the bigger K of LnL_3phen the bigger k of the reaction of forming LnL_3phen [6].

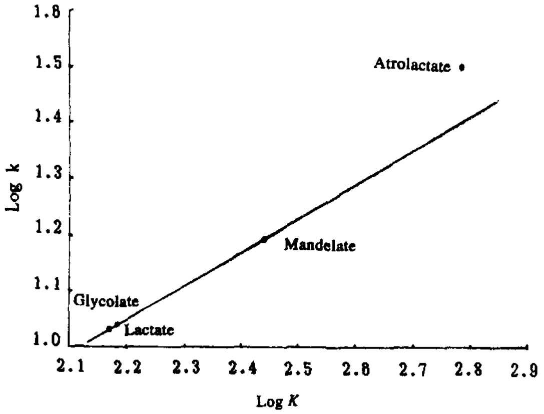

Fig. 1. Log k values of the reactions of the La-hydroxycarboxylate with phen plotted against the log K values of the La^{III} ternary complex.

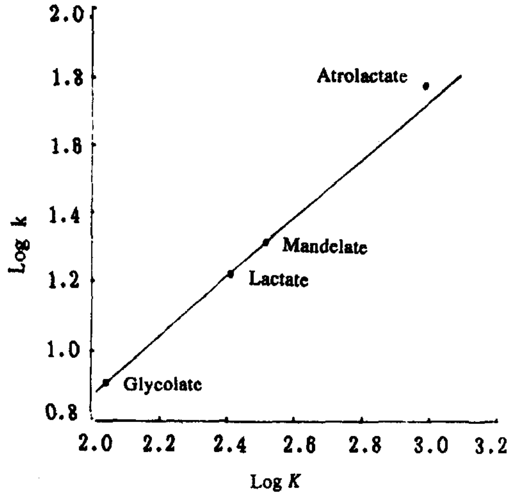

Fig. 2. Log k values of the reactions of the Eu-hydroxycarboxylate with phen plotted against the log K values of the Eu^{III} ternary complex.

The order of acid dissociation constants was reported as mandelic acid (pK_a 3.41) > atrolactic acid > glycollic acid (pk_a 3.83) > lactic acid (pK_a 3.86). It is further observed that a linear free energy relationship exists between the rate constants of the reaction $[LaL_3(H_2O)_2 + phen = LaL_3phen + 2H_2O]$ and the acid strengths of α-hydroxy-acid as primary ligand [7]. However the linear free energy relationship does not exist between the rate constants of the reaction $[EuL_3(H_2O)_2 + phen = EuL_3phen + 2H_2O]$ and the acid strength (pK_a) of α-hydroxy-acid. This is probably because of the difference between the La^{III} and Eu^{III} character.

In addition, as seen from Figs 1 and 2, the reaction of $Ln(C_6H_5CH_3COHCOO)_3(H_2O)_2$ with phen is not in agreement with the linear free energy relationship. This is due to the configuration of solvation of $Ln(C_6H_5CH_3COHCOO)_3(H_2O)_2$ differs from the other lanthanide α-hydroxycarboxylates [3]. The $C_6H_5CH_3COHCOO^-$ of $Ln(C_6H_5CH_3COHCOO)_3(H_2O)_2$ having the most volumetrical effect that could shield lanthanide ions from combining with solvent molecules. Thus, the degree of solvation of $Ln(C_6H_5CH_3COHCOO)_3(H_2O)_2$ is lower than that of $Ln(CH_2OHCOO)_3(H_2O)_2$, $Ln(CH_3CHOHCOO)_3(H_2O)_2$ and $Ln(C_6H_5CHOHCOO)_3(H_2O)_2$ ($Ln = La^{III}, Eu^{III}$), the number of molecules of solvation is small and is favourable for the coordination of two nitrogen atoms of phen.

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