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STUDIES ON THE KINETICS OF COMPLEXATION OF SEVEN LANTHANIDE MANDELATES WITH 1, 10 – PHENANTHROLINE

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ABSTRACT

The kinetics of the coordination reaction of seven lanthanide(III) (La, Ce, Pr, Nd, Sm, Eu and Gd) mandelates, $LnL_3(H_2O)_2$, with 1, 10-phenanthroline (phen) in methanol-water (3:2 v/v) were studied at 25° C by calorimetric titration. We have evaluated the rate constants of the reactions. A two-steps reaction process in accordance with the rate equation is suggested. The reaction is first-order each in lanthanide mandelate and phen. The variation rule of the rate constants with the atomic numbers or the ionic radii of the lanthanide ions is discussed. It is found that a linear free energy relationship does not exist between the stability constants of the lanthanide-mandelate-phen ternary complex and the rate constants. The influence of other factors upon the reaction rate is also discussed.

INTRODUCTION

Mandelic acid and its lanthanide complexes have been extensively investigated[1,2]. In our previous work[3,4], we have reported the synthesis, properties and proposed structure (as shown in Fig. 1) of the ternary solid complexes (LnL_3phen) of lanthanides with mandelic

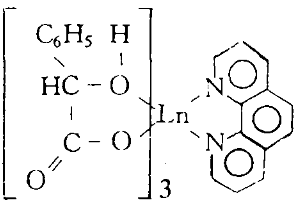

Fig. 1. The Proposed Structure of LnL_3 phen

(Ln = La, Ce, Pr, Nd, Sm, Eu and Gd, L = $C_6H_5CHOHCOO^-$)

acid and 1,10-phenanthroline (phen). We have also reported the thermodynamic properties of the complexes of the lanthanide mandelates with phen in methanol-water (3:2 v/v) as determined at 25° C by calorimetric titration. This study included a discussion on the variation rule of thermodynamic properties with the atomic numbers or the ionic radii of the lanthanide ions. In addition, we have reported the kinetics of the coordination reaction of lanthanide α-hydroxycarboxylates with phen including a discussinon of the influence of several factors upon the reaction rate[5]. We now report the kinetics of the chemical reaction of lanthanide mandelates with phen.

RESULTS AND DISCUSSION

In continuous titration calorimetry, the stoichiometric reaction which has been confirmed by our previous studies[3,4] in this experiment can be represented as:

$$A + B \rightarrow AB \quad (1)$$

where A represents the titrant phen, B represents the titrate[2] $LnL_3(H_2O)_2$ and AB represents the resultant[4] LnL_3phen (omitting the resultant H_2O). Eleven data points at 11 min intervals were used in the calculation. The concentration of the various species in the calorimeter at the end of the time intervals (any point p) can be calculated by using eqns. (2) - (6)

$$K=\frac{[AB]_p}{[A]_p[B]_p} \quad (2)$$

$$[A_T]_p=[A]_p+[AB]_p \quad (3)$$

$$[B_T]_p=[B]_p+[AB]_p \quad (4)$$

$$K=[AB]_p/([A_T]_p-[AB]_p)([B_T]_p-[AB]_p) \quad (5)$$

$$K[AB]_p^2-(K[B_T]_p+K[A_T]_p+1)[AB]_p+K[A_T]_p[B_T]_p=0 \quad (6)$$

where K is the thermodynamic equilibrium constant. [A], [B] and [AB] represent the concentration of the components A, B and AB, respectively. $[A_T]$ and $[B_T]$ represent the total concentration of A and B in the reaction vessel, respectively . The initial concentrations of A_T and B_T are known and as the titration proceeds $[A_T]_p$ and $[B_T]_p$ can be calculated at the end of each time interval[6].

To calculate the concentrations of the species in the system at the end of each time interval, a value of K is assumed and using the appropriate values of $[A_T]_p$ and $[B_T]_p$, the values of $[AB]_p$, $[A]_p$ and $[B]_p$ are calculated from eqns. (6), (3) and (4), respectively. In this experiment, only the concentration of $[AB]_p$ is necessary to complete the calculation. The concentrations of $[AB]_p$ were printed by using a TP-801 computer (see Table I).

In the experiment, the concentrations of phen (A) and $LnL_3(H_2O)_2$ (B) are almost the same, so we assumed that the rate equation of the reactions mentioned above can be expressed as shown in eq. (7)

$$r=k[\text{phen}]^x[LnL_3(H_2O)_2]^y \quad (7)$$

where k is the rate constant of the reactions, L represents $C_6H_5CHOHCOO^-$ and Ln represents La(III), Ce(III), Pr(III), Nd (III), Sm(III), Eu(III), and Gd(III).

Assuming x = y = 1, plots of $\log \frac{[B_T]}{[A_T]}\frac{[A_T]-[AB]_p}{[B_T]-[AB]_p}$ against time (t) are straight lines supporting the assumption x = y = 1. It is

Table I. The Concentrations of $Sm(C_6H_5CHOHCOO)_3phen$ ($[AB]_p$, given in mol dm^{-3}) Present in the Reaction Vessel of a 0.004793 mol dm^{-3} phen ($[A_T]$) with a 0.001979 mol dm^{-3} $Sm(C_6H_5CHOHCOO)_3(H_2O)_2$ ($[B_T]$) at 25° C in Methanol-Water (3:2 v/v)

Time (min)	$[AB]_p$	$[A_T]-[AB]_p$	$[B_T]-[AB]_p$	$\log \frac{[B_T]}{[A_T]} \frac{[A_T]-[AB]_p}{[B_T]-[AB]_p}$
1.00	0.0001899	0.0046031	0.0017891	0.026
2.00	0.0003566	0.0044364	0.0016224	0.053
3.00	0.0005020	0.0042910	0.0014770	0.079
4.00	0.0006284	0.0041646	0.0013506	0.105
5.00	0.0007379	0.0040551	0.0012411	0.130
6.00	0.0008328	0.0039602	0.0011462	0.154
7.00	0.0009151	0.0038779	0.0010639	0.178
8.00	0.0009864	0.0038066	0.0009926	0.200
9.00	0.0010484	0.0037446	0.0009306	0.220
10.00	0.0011024	0.0036906	0.0008766	0.240
11.00	0.0011495	0.0036435	0.0008295	0.259

proven that the reaction is first-order each for lanthanide mandelate and phen, and the rate equation is $r = k[phen][LnL_3(H_2O)_2]$. The rate constants can be calculated from the slopes of the lines. The values of the observed rate constants of the above reactions are summarized in Table II.

As seen in Table II, the values of the observed rate constants of the reactions are low. This is because the intermolecular hydrogen bond of $LnL_3(H_2O)_2$ with the solvent H_2O molecules is not favorable for the coordination of the nitrogen atoms of phen. Furthermore, the steric hindrance of phen due to its rigid structure is also not favorable for the coordination of phen.

Table II. Observed Rate Constants[a] and Equilibrium Constants[4] for the Complexation of Seven Lanthanide Mandelates with phen in Methanol-Water (3:2 v/v) at 25° C

Complex	Cation atomic number	Ionic radius (Å)	k (mol^{-1} dm^3 min^{-1})	Log k	Log K
$La(C_6H_5CHOHCOO)_3phen$	57	1.061	15.51 ± 0.01	1.19	2.44
$Ce(C_6H_5CHOHCOO)_3phen$	58	1.034	20.39 ± 0.03	1.31	3.15
$Pr(C_6H_5CHOHCOO)_3phen$	59	1.013	22.54 ± 0.01	1.35	3.27
$Nd(C_6H_5CHOHCOO)_3phen$	60	0.995	24.59 ± 0.03	1.39	3.65
$Sm(C_6H_5CHOHCOO)_3phen$	62	0.964	21.40 ± 0.09	1.33	2.68
$Eu(C_6H_5CHOHCOO)_3phen$	63	0.950	20.65 ± 0.03	1.32	2.51
$Gd(C_6H_5CHOHCOO)_3phen$	64	0.938	20.54 ± 0.06	1.31	2.33

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

It is further observed that the observed rate constants of the reaction of $LnL_3(H_2O)_2$ with phen increase from La(III) to Nd(III), that is, with the increase of the atomic number. This definitely proves that the ion volume effect plays a predominant role. When La(III), Ce(III), Pr(III), and Nd(III) are coordinated to mandelic acid to form $LnL_3(H_2O)_2$, there is still suitable space to coordinate with phen. Thus, for the lanthanides from La(III) to Nd(III), the observed rate constant and its variation depends on the size of the lanthanide ion. With the further decrease of ionic radii of lanthanide ions after Nd (III), the relatively small space around the lanthanide ion in $LnL_3(H_2O)_2$ and the increase of the solvation of $LnL_3(H_2O)_2$ are not favorable for the coordination of phen. These effects are responsible for the decrease in the rate constants of the reactions of $LnL_3(H_2O)_2$ with phen.

Based on the structural characteristics of the reactants, the products and the above discussion, the probable reaction mechanism can be expressed by eqs. (8) and (9).

$$LnL_3(H_2O)_2 \xrightarrow{k} LnL_3 + 2H_2O \qquad \text{(slow reaction)} \qquad (8)$$

$$LnL_3 + phen \xrightarrow{k'} LnL_3phen \qquad \text{(fast reaction)} \qquad (9)$$

The rate-determining step is the first step. This is because the Ln-OH_2 bonds in $LnL_3(H_2O)_2$ don't break easily. The second step is a fast reaction because of chelation acceleration. So the formation of the chelate can be treated as a steady state as follows:

$$\frac{d[LnL_3]}{dt} = k[LnL_3(H_2O)_2] - k'[LnL_3] = 0 \qquad (10)$$

$$\frac{d[LnL_3phen]}{dt} = k'[LnL_3][phen] \qquad (11)$$

The rate equation, in accordance with the two-steps process, is given in eq. (12).

$$\frac{d[LnL_3phen]}{dt} = k[LnL_3(H_2O)_2][phen] \qquad (12)$$

which is in agreement with the previous assumption.

For different lanthanides, it is found that the larger the K the larger is the k of the reaction of forming LnL_3phen. This means, the more stable the complexes, the faster is the rate of formation of the complexes[7]. But a linear free energy relationship does not exist between the reaction rate constants (log k) and the stability constants (log K). This is because the different solvation of $LnL_3(H_2O)_2$ owing to the difference of the Ln(III) character, give rise to the different k values.

On the basis of our previous work[5] and the above discussion, we come to the conclusion that for a given lanthanide and different α-hydroxycarboxylates or a given α-hydroxycarboxylate and different lanthanides, the reaction process is the same, which is due to the similar structure and nature of the different α-hydroxycarboxylates or the different lanthanides. But the reaction rate of different reactions mentioned above is different indicating the different character of different α-hydroxycarboxylates or lanthanides.

Several factors such as temperature, concentration, which may influence the reactions of lanthanide α-hydroxycarboxylates with phen have not been examined. However, the present work appears to demonstrate that the dominant factor controlling the reaction rate is the nature of the lanthanide and the α-hydroxycarboxylate itself.

EXPERIMENTAL

Reagents and Apparatus

The reagents and the apparatus employed were the same as reported earlier[4]. The composition of the reactant, $LnL_3(H_2O)_2$, and the resultant, LnL_3phen, were confirmed by elemental analyses. The structures of $LnL_3(H_2O)_2$ and LnL_3phen were investigated using IR, TGA, UV and X-ray powder diffraction[2,3].

Experimental Procedure and Calculation Methods

The detailed experimental procedure and the method used for calculating the concentration of the species present in the reaction vessel were similar to those described previously[5,6].

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