Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 269 (2007) 104–109
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Study on kinetics and mechanism of mononuclear rare earth metal complexes in promoting the hydrolysis of 2-hydroxy-propyl-*p*-nitrophenyl phosphate (HPNP)

Qiang Liu [a], Huamei Chen [a], Hai Lin [b], Huakuan Lin [a,*]

[a] *Department of Chemistry, Nankai University, Tianjin 300071, PR China*
[b] *State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Nankai University, Tianjin 300071, PR China*

Received 27 October 2006; accepted 16 November 2006
Available online 24 November 2006

Abstract

Two novel tripodal ligands, *N*,*N*′,*N*″-tri-(3′-phenylpropionic acid-2′-yl)-1,3,5-tri-aminomethylbenzene (L1), *N*,*N*′,*N*″-tri-(4′-methylvaleric acid-2′-yl)-1,3,5-triamino-methylbenzene (L2) have been synthesized. The hydrolytic kinetics of 2-hydroxy-propyl-*p*-nitrophenyl phosphate (HPNP) catalyzed by complexes of L1, and L2 with La(III) and Gd(III) have been studied in aqueous solution at 298 K, $I = 0.10$ mol dm^{-3} KNO_3 at pH 6.7–8.2, respectively. GdL2 has the best catalytic effect in the four complexes for hydrolysis of HPNP. Its k_{LnLH-1}, k_{LnL} and pK_a are 0.0927 mol^{-1} dm^3 s^{-1}, 0.000101 mol^{-1} dm^3 s^{-1} and 7.73, respectively. Due to smaller radius of Gd(III) compared with that of La(III), its complexes have lower pK_a and better catalytic ability compared with corresponding La(III) complexes. This paper expounds the result from the structure of the ligands and the properties of the metal ions, and deduces the catalysis mechanism.

Keywords: Mechanism; Rare earth; Kinetics; Hydrolysis; 2-Hydroxy-propyl-*p*-nitrophenyl phosphate

1. Introduction

Mimic enzyme is a kind of compound artificially synthesized based on the understanding of the structure of the enzymes and the reaction mechanism and having specific attribute for hydrolysis biological macromolecules. The character of the mimic enzymes is small molecule and simple structure. However, they have the active groups and spacial structure similar to the groups that nature enzymes have.

There are many hydrolytic enzymes in the process of organic evolution, for example carbonic anhydrase, carboxypeptidase, alkaline phosphatase and so on. They take part in the hydrolysis of some very important organic molecular and take an important role in the process of life [1].

The reaction mechanism of hydrolase and the effect of the metal ions in the active center are always important in bioinorganic chemistry field [2]. Recently there have been many research efforts to design and synthesize model complexes for promoting the hydrolysis of 2-hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) [3]. Ligands containing more amino groups and more carboxyl groups or ligands bearing multi-ions are potentially useful to achieve more active molecular catalysts. In this paper, it is studied that the property of hydrolysis of HPNP for the complexes of *N*,*N*′,*N*″-tri-(3′-phenylpropionic acid-2′-yl)-1,3,5-triaminomethylbenzene(L1), *N*,*N*′,*N*″-tri-(4′-methylvaleric acid-2′-yl)-1,3,5-triaminomethylbenzene (L2) with La(III) and Gd(III), respectively. Our interest was to understand functions of metal ions in biological hydrolysis process.

2. Experimental

2.1. Materials

All reagents and solvents were of analytical reagent grade and were used without further purification, unless otherwise noted. All aqueous solutions were prepared using redistilled water. Metal ion stock solutions were prepared from their respective salts and were titrated against EDTA following standard procedures. The buffer component tris(hydroxymethyl)

* Corresponding author. Tel.: +86 22 23502624; fax: +86 22 23502458.
E-mail address: hklin@nankai.edu.cn (H. Lin).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.11.033

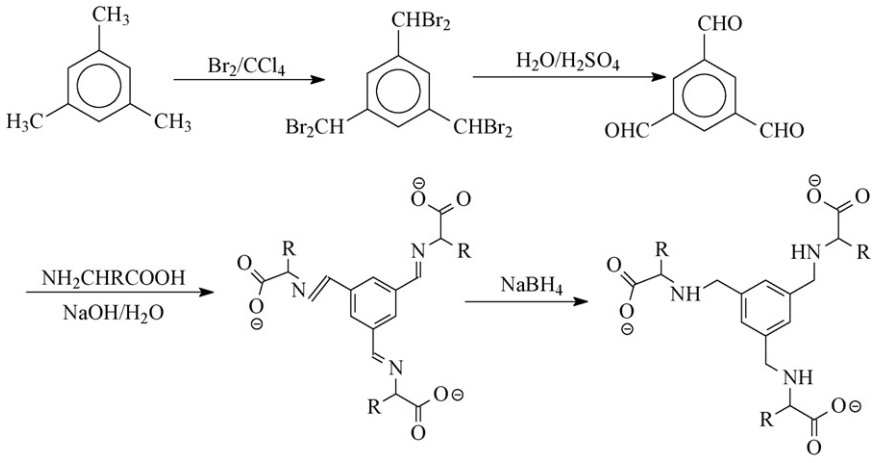

Fig. 1. The process of the preparation of ligands (L1 = $C_6H_5CH_2$–, L2 = $(CH_3)CHCH_2$–).

aminomethane (Tris) was used as supplied by the manufacturer. The 2-hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) were prepared and purified as a barium salt following literature methods [4,5]. *N*,*N*′,*N*″-Tri-(3-phenylpropionic acid-2′-yl)-1,3,5-triaminomethylbenzene (L1), *N*,*N*′,*N*″-tri-(4′-methylvaleric acid-2′-yl)-1,3,5-triaminomethylbenzene (L2) were synthesized following literature methods [6] and the process of synthesis was shown in Fig. 1.

2.2. Potentiometric determination

Potentiometric determination was measured in a 50 cm^3 jacketed cell thermostated at 298.2 ± 0.1 K by a refrigerated circulating water bath. Anaerobic condition were maintained using pre-purified N_2 as an inert atmosphere, and the ionic strengths were maintained by adding KNO_3 to achieve $I = 0.1$ mol dm^{-3}. The calibration of the glass electrode was the same as described in the literature [7]. In a typical experiment, the ligand was dissolved in an adequate amount of dilute HNO_3 and then titrated with 0.1 mol dm^{-3} KOH. The values of $k_w = 1.008 \times 10^{-14}$, $\gamma_{H^+} = 0.825$ of water were used for the calculations. The calculations were carried out by SCMAR program [8] based on the improved TITFIT technique [9]. (Program SCMAR and TITFIT are two programs for the calculation of cumulative formation constants from potentiometric data.) The final results were the averages of three independent titrations, each titration containing about 70 experimental points.

2.3. Kinetics of HPNP hydrolysis

A kinetic study was carried out by the UV–vis spectra method using a Beckman DU-8B spectrophotometer equipped with a thermostat cell holder. The hydrolysis rate of HPNP in aqueous solution was measured by an initial slope method following the increase in absorption at 400 nm due to the release of 4-nitrophenolate. The reaction solution was maintained at 298 K and the ionic strength was adjusted to 0.10 mol dm^{-3} with KNO_3. The buffer component tris(hydroxymethyl)aminomethane (tris) was used to maintain pH, and it do not coordinate with Ln(III) ions under this condition. For the initial rate determination, the following typical procedure was employed.

After HPNP and the Ln(III) complexes solution at the appropriate pH were mixed, the UV absorption increase was recorded immediately (the reference experiment did not contain the catalyst). The increase in concentration of *p*-nitrophenolate was measured every 60 s. The initial slope (<5% conversion) of a plot of the measured absorbance versus time was determined (correlation coefficient > 0.99). All the experiments were in triplicate and the tabulated data represent the average of these experiments.

3. Results and discussion

3.1. Active nucleophile in 1:1 Ln/L systems

The stepwise protonation constants of L_1 and L_2 are shown in Table 1, respectively. Potentiometric titration indicated that the complexes formed by La(III) and Gd(III) with L_1 and L_2 are performed at 1:1 metal–ligand molar ratios, respectively. The stability constants of $LnLH_m$ ($m = 2$ to -1) complexes in the 1:1 ratio are in Table 2. From the species percentage distribution diagrams of Ln–L binary system (Fig. 2) it is find that the mode $LnLH_{-1}(1,1,-1)$ (L = L1 or L2) having ability to catalyze hydrolysis of HPNP is formed in the solution when pH > 7.0.Therefore the kinetic experiment would be carried out in pH 6.7–8.2.

The deprotonation constants of coordination water on LnL (1 1 0) can be obtained according to $pK_a = \log \beta_{LnL} - \log \beta_{LnLH-1}$ shown in Table 3. LnL(1 1 0) can release a proton to give $LnLH_{-1}$ at weak basic (pH > 7.0) solution which is a good

Table 1
The protonation constants of ligands L_1 and L_2 (pH range 2.5–10.8, 298 ± 0.1 K, $I = 0.1$ mol dm^{-3} KNO_3, $C_L = 5 \times 10^{-4}$ mol dm^{-3})

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log K_1$	$\log K_2$	$\log K_3$
L1	9.23	17.71	25.36	9.23	8.48	7.65
L2	9.82	19.04	26.95	9.82	9.22	7.91

Table 2
The stability constants of binary complexes of ligands L1, L2 with La(III), Gd(III) $C_L = C_{Ln} = 5 \times 10^{-4}$ mol dm^{-3}, $I = 0.1$ mol dm^{-3} KNO_3, 298 ± 0.1 K

	Complexes	La(III)	Gd(III)
L1	$\log \beta_{112}$	22.48	23.83
	$\log \beta_{111}$	14.39	16.71
	$\log \beta_{110}$	7.14	8.98
	$\log \beta_{1,1,-1}$	−0.76	1.32
	$\log \beta_{1,1,-2}$	−9.57	−7.35
	$\log \beta_{1,1,-3}$	−18.85	−16.62
	$\log \beta_{1,1,-4}$	−28.80	−26.54
L2	$\log \beta_{112}$	24.14	26.48
	$\log \beta_{111}$	16.34	19.30
	$\log \beta_{110}$	9.54	12.41
	$\log \beta_{1,1,-1}$	1.68	4.56
	$\log \beta_{1,1.-2}$	−6.90	−3.48
	$\log \beta_{1,1,-3}$	−16.50	−12.81
	$\log \beta_{1,1,-4}$	−26.27	−22.41

nucleophilic metal-bond hydroxide specie and they can be used as enzyme models for catalyzing the hydrolysis of phosphate diester HPNP because of their nucleophilic group OH^-.

3.2. Molar extinction coefficient of NP^-

The kinetic study of HPNP hydrolysis was carried out by monitoring the amount of *p*-nitrophenolate ion (NP^-) produced in solution at 400 nm. The use of buffer for the studies of hydrolysis kinetics of HPNP was required since the change of pH value of the solution would cause change of the concentration of the NP^-. To determine the rate constants one should know the molar extinction coefficient of NP^-, which varies considerably with pH values of the solution. In solution *p*-nitrophenol dissociate as following:

$$HNP = H^+ + NP^- \quad (1)$$

$$K_a = \frac{[NP^-][H^+]}{[HNP]} \quad (2)$$

According to Beer's law,

$$A = \varepsilon_{obs} b [HNP]_T = \varepsilon_{NP} b [NP] \quad (3)$$

where ε_{obs} is the observed extinction coefficient of HNP, ε_{NP} the extinction coefficient of the NP^- anion, b the cell length, and A is the absorption of the samples. From Eqs. (2)–(5) are obtained:

$$\varepsilon_{obs} = \frac{\varepsilon_{NP} K_a}{K_a + [H^+]} \quad (4)$$

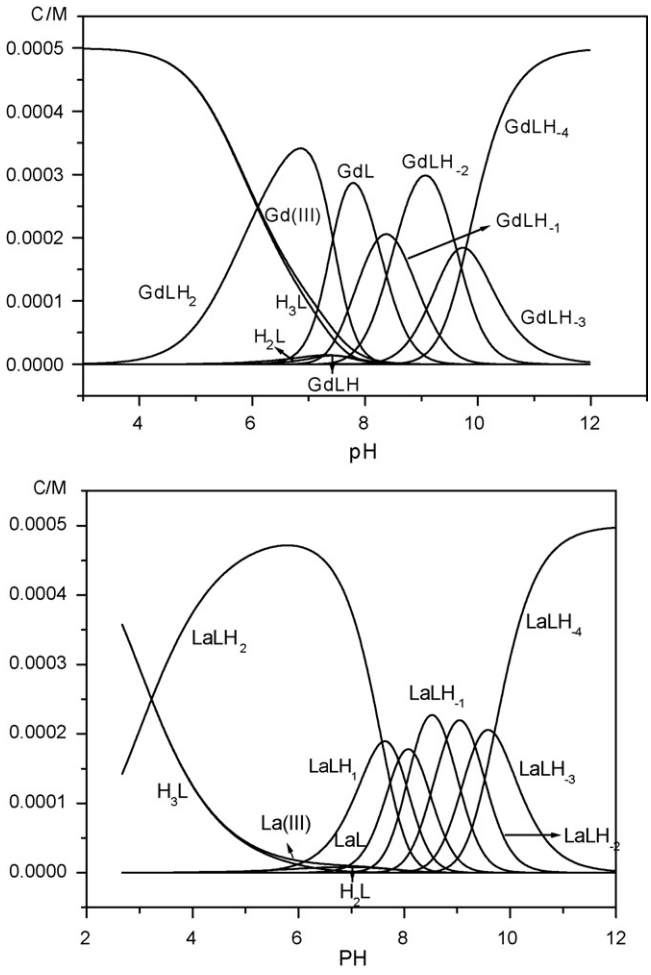

Fig. 2. The species percentage distribution diagrams of Gd(III)-L1, La(III)L1 binary system (298.2 K, $I = 0.1$ mol dm^{-3} KNO_3, $C_{L1} = C_{Gd} = 5 \times 10^{-4}$ mol dm^{-3}).

$$\frac{1}{\varepsilon_{obs}} = \frac{1}{\varepsilon_{NP}} + \frac{[H^+]}{\varepsilon_{NP} K_a} \quad (5)$$

With the plot of $1/\varepsilon_{obs}$ versus $[H^+]$, the molar extinction coefficient ε_{NP} and the dissociation constant of *p*-nitrophenol K_a at 400 nm in 0.020 mol dm^{-3} Good's buffers were obtained with the values of 17900 mol^{-1} dm^3 cm^{-1} and 7.66×10^{-8} mol dm^{-3}, respectively, which is consistent with the reported value [10].

3.3. Kinetic studies of hydrolysis of HPNP

Under the experimental conditions, the hydrolysis rate increases linearly with the increase of HPNP concentration,

Table 3
The second-order rate constants k_{LnL}, k_{LnLH-1} and the deprotonation constant of water coordinated on LnL pK_a^2 in the hydrolysis of HPNP

Complexes	10^2 k_{LnL} (mol^{-1} dm^3 s^{-1})	K_{LnLH-1} (mol^{-1} dm^3 s^{-1})	pK_a (titration)	pK_a
LaL1	0.0026	0.0341	7.90	7.92
LaL2	0.0031	0.0434	7.86	7.84
GdL1	0.0067	0.0753	7.66	7.71
GdL2	0.0101	0.0927	7.76	7.73

Table 4
The apparent rate constants catalyzed hydrolysis of HPNP by Ln–L complexes, k_{cat}^{obs}, at different pH values

pH	$[H^+]$ ($\times 10^{-8}$ mol dm^{-3})	k_{cat}^{obs} (mol dm^{-3} s^{-1})			
		LaL1	LaL2	GdL1	GdL2
6.721	23.15	0.001792	0.002573	0.006564	0.006577
7.074	10.22	0.003761	0.005394	0.013353	0.02356
7.285	6.29	0.005705	0.007899	0.019563	0.020148
7.564	3.31	0.00941	0.012799	0.030081	0.033982
7.851	1.71	0.014468	0.019407	0.042496	0.046776
8.138	0.88	0.020075	0.02652	0.053721	0.062574

which indicates that the hydrolysis is first-order with respect to HPNP, and can be written in the following form:

$$V = \frac{dA}{\varepsilon\, dt} = k_{obs}[HPNP]$$
$$= (k_{cat}^{obs}[complex]^T + k_{OH}[OH] + k_0)[HPNP] \quad (6)$$

where V is the hydrolysis rate, k_{obs} the observed rate constant, and k_{obs} includes all the catalytic species, such as the Ln–L complexes, base (OH^-) and other species (solvent H_2O). Therefore, k_{obs} can be written:

$$k_{obs} = k_{cat}^{obs}[complex]^T + k_{OH}[OH^-] + k_0 \quad (7)$$

where k_{cat}^{obs} and k_{OH} are the apparent catalytic rate constants of Ln–L complexes and OH^-, respectively, and k_0 is constant probably due to the solvolysis of HPNP (i.e. water attack on the diester). At a given pH, when the observed hydrolysis rate constant, k_{obs}, was plotted against total concentration of complexes Ln–L, the apparent rate constant of complexes, k_{cat}^{obs}, can be obtained. Table 4 shows the apparent hydrolysis rate constant, k_{cat}^{obs}, at different pH. As shown in Table 3, the apparent hydrolysis rate constant of complexes Ln–L, k_{cat}^{obs}, increases with the increase of the pH value of reaction solution. When the total apparent hydrolysis rate constant of complexes Ln–L, k_{cat}^{obs}, is plotted against pH, resulting curve indicate the characteristics of a kinetic process controlled by acid–base equilibrium (due to deprotonation of the coordination water on complex LnL) (see Fig. 3). In Eq. (7) $[complex]^T$ is the total concentration

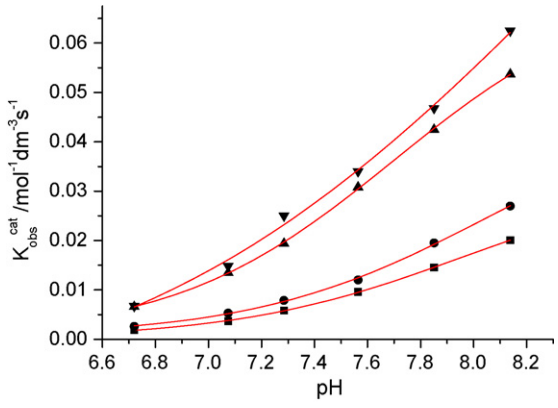

Fig. 3. The curve of relation of apparent hydrolysis rate constant of HPNP, k_{cat}^{obs} vs. pH catalyzed by complexes Ln–L. (■) LaL1; (●) LaL2; (▲) GaL1; (▼) GaL2.

of Ln–L complexes. As discussed earlier, there are two types of nucleophile in the 1:1 system: LnL and $LnLH_{-1}$, with the equilibrium constant pK_a^2 ($pK_a^2 = \log\beta_{110} - \log\beta_{11-1}$). The concentrations of LnL and $LnLH_{-1}$ have been controlled by pH value of the reaction solution and can be represented by Eqs. (8) and (9):

$$[LnL] = \frac{[complex]^T[H]}{K_a^2 + [H]} \quad (8)$$

$$[LnLH_{-1}] = \frac{[complex]^T K_a^2}{K_a^2 + [H^+]} \quad (9)$$

According to kinetics theory of enzumatic catalysis, Eq. (10) is then obtained

$$k_{cat}^{obs}[complex]^T = k_{LnL}[LnL] + k_{LnLH-1}[LnLH_{-1}] \quad (10)$$

where k_{LnL} and k_{LnLH-1} stand for the second-order hydrolysis rate constants of HNPH catalyzed by LnL and $LnLH_{-1}$, respectively. Eq. (11) could be obtained from Eqs. (8)–(10):

$$k_{cat}^{obs} = \frac{k_{LnL}[H] + k_{LnLH-1}K_a^2}{[H] + K_a^2} = \frac{k_{LnL} + (k_{LnLH-1} - k_{LnL})}{1 + [H]^+/K_a^2} \quad (11)$$

Thus, by means of non-linear least-squares fit of k_{cat}^{obs} versus $[H^+]$, the values of k_{LnL}, k_{LnLH-1} and K_a^2 can be obtained according to Eq. (11). From Table 3 it could be found that dissociation constants of coordination water on complex LnL (pK_a^2) got from the kinetic experiment is consistent with the result got from the titration experiment.

As a rule, in the species LnL the coordinated water is the nucleophilic group, while the hydroxyl group, OH^- is the nucleophilic group in the species $LnLH_{-1}$.

There is a nucleophilic group R-OH in HPNP, so its hydrolysis mode is somewhat different from other diesters.

From the data in the Tables 3 and 4, the mechanism of the catalysis of hydrolysis of HPNP can be deduced (Fig. 4). From the data in Table 4, the total apparent rate constant (k_{cat}^{obs}) of hydrolysis of HPNP catalyzed by Ln–L binary system complexes increase with the increase of pH value of reaction solution. This phenomenon is same with one reported Richard [3], it is interesting that ionization of mononuclear rare earth complex LnL at the solution of weak basic pH is due to loss of a proton from a water bound on Ln(III) of complex LnL, because the pH-rate profiles show that the ionization state of the water bound on

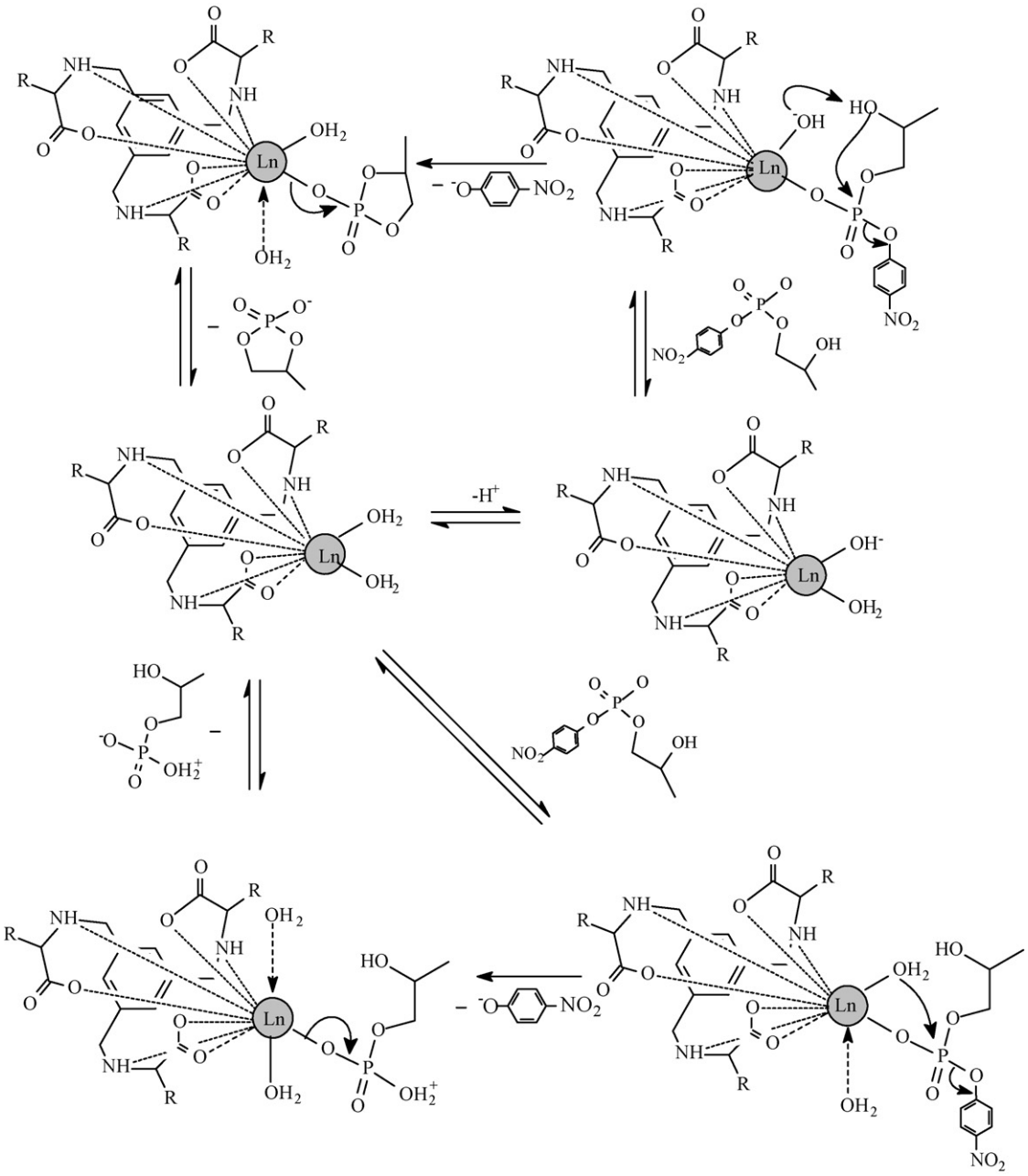

Fig. 4. The mechanism of the catalyzed the hydrolysis of HPNP.

Ln(III) of complex LnL is critical for catalytic activity. The pH-rate profiles of the second-order rate constants k_{cat}^{obs} for catalysis of transesterification of HPNP by Ln–L provide the following important insights into catalytic reaction mechanism.

There is a downward break in the pH-profile for the hydrolysis of HPNP catalyzed by Ln–L complex system that is centered at pK_a^2 for deprotonation of a bound water molecule to form the monohydroxyl complex $LnLH_{-1}$. The pH-rate profile shows that the complex LnL is less active species catalyzed hydrolysis of HPNP than $LnLH_{-1}$ and is converted to a more active form $LnLH_{-1}$ upon loss of a proton. Jencks considered that kinetics provides no information about whether this proton is lost from catalyst or substrate [11]. However, Richard Wolfenden, [12] consider that chemical logic demands that a proton be lost from the C2-hydroxyl of HPNP on proceeding from reactant in solution to the transition state for transesterification and that the catalyst functions in some way to facilitate ionization of this hydroxyl. Richard [3] consider that there are two possible pathways for activation of HPNP by direct proton transfer from the C2-hydroxyl to the catalyst: (a) $Zn_2(L2O)(OH)$ and $Zn(L1OH)(OH)$ may serve as the active form of the catalyst and act as Bronsted general base catalysts to deprotonate the C2-hydroxyl of HPNP in reactions where proton transfer to the catalyst is concerted with intramolecular addition of C2-oxygen to the phosphate diester. (b) Proton transfer from substrate to the ionized catalysis $Zn_2(L2O)(OH)$ or $Zn(L1OH)(OH)$ may occur as a pre-equilibrium step to form the protonated catalysis $Zn_2(L2O)(H_2O)$ and $Zn(L1OH)(H_2O)$, respectively, and the C2-

oxyanion of substrate which would then undergo intramolecular nucleophile addition to phosphate diester.

We consider that the lost proton related with a downward break in the pH-rate profile come from the water molecule coordinated on Ln(III) of the complex LnL, because the pK_a of free water at 298.2 K is about 14 and the pK_a of isopropyl alcohol at 298.2 K is about 16. When water molecule coordinated with Ln(III) in complex LnL, electron-withdraw effect of Ln(III) in complex will significantly decrease the pK_a of coordinated water. While C2-hydroxylpropyl of substrate, if not coordinated to metal via hydroxyl oxygen, its pK_a should still keep at ~16 due to it is far away from metal ion compared with coordinated water molecule. The complex LnL lost the proton of coordinated water and change into the complex $LnLH_{-1}$ then the coordinated hydroxyl group of the complex $LnLH_{-1}$ attack the C2-hydroxypropyl of substrate. The proton releasing from the coordination water on complex LnL decreased the pH value of reaction solution as expected. The proton of C2-hydroxypropyl transfer to the hydroxyl group of complex $LnLH_{-1}$ with intramolecular attack of C2-oxyanion to the phosphate diester immediately. This transferring proton cannot cause a change of pH value of the reaction solution. From Table 3 it could be found that dissociation constants of coordination water on the complex LnL (pK_a^2) got from the kinetic experiment was consistent with the result got from the titration experiment. This is a powerful evidence of our viewpoint.

HO^- coordinated on Ln(III) of complex $LnLH_{-1}$ attacks the hydroxyl group of C2-hydroxypropyl of HPNP. H^+ of hydroxyl group of C2-hydroxypropyl of HPNP transfer to OH^- coordinated on Ln(III) of complex $LnLH_{-1}$ and itself change into C2-oxyanion. Then C2-oxyanion with intramolecular addition attacks P atom of HPNP. This result leads *p*-nitrophenate ion leave from HPNP. H_2O coordinated on Ln(III) in complex LnL can directly attack P atom of HPNP and lead *p*-nitrophenate ion leave from HPNP. Because the electron cloud density on C2-oxyanion is much higher than one on oxygen atom of H_2O coordinated on Ln(III), therefore, k_{LnLH-1} is much larger than k_{LnL}.

The second-order rate constant k_{Zn}, for transesterification of HPNP catalyzed by $Zn_2\{L2O\}$ and Zn(L1OH) at 298 K, $I = 0.1\ mol\ dm^{-3}$ $NaNO_3$ and $20\ mmol\ dm^{-3}$ buffer increase with the increase of pH value of reaction solution as reported by Richard. As rule, when the temperature and the medium of reaction solution was confirmed the rate constant of a reaction is fixed. Rate constants depend only on temperature and medium. Second-order rate constants, k_{Zn}, increase with the increase of pH value of reaction solution reported by Richard [3], in our opinion, is only apparent second-order rate constants at a given pH ($k_{Zn} = 0.25\ mol^{-1}\ dm^3\ s^{-1}$ for complex $Zn_2\{L2O\}$ and $k_{Zn} = 0.0013\ mol^{-1}\ dm^3\ s^{-1}$ for complex Zn(L1OH) at pH 7.6). They did not obtained true second-order rate constant of complexes $Zn_2(L2O)(OH)$, $Zn_2(L2O)(H_2O)$ and Zn(L1OH)(OH), $Zn(L1OH)(H_2O)$. If by means of non-linear least-squares fit of k_{Zn} versus $[H^+]$ according to Eq. (11), the values of $k_{Zn_2(L2O)(OH)}$, $k_{Zn_2(L2O)(H_2O)}$ and $k_{Zn(L1OH)(OH)}$, $k_{Zn(L1OH)(H_2O)}$ can be obtained. Though Richard et al. did not obtain that the true second-order rate constants of hydrolysis of HPNP catalyzed by complex $Zn_2(L2O)(OH)$, $Zn_2(L2O)(H_2O)$ and Zn(L1OH)(OH), $Zn(L1OH)(H_2O)$, $k_{Zn_2}(L2O)(OH)$, $k_{Zn_2}(L2O)(H_2O)$ and $k_{Zn(L1OH)(OH)}$, $k_{Zn(L1OH)(H_2O)}$, we can still compare of the activity of hydrolysis of HPNP catalyzed by the complexes Ln–L designed and synthesized in this work with one catalyzed by the complexes $Zn_2(L2O)$, Zn(L1OH) designed and synthesized in Richard's work simply by compare the data in Tables 3 and 4. From the data in Tables 3 and 4, it is found that the activity of hydrolysis of HPNP catalyzed by the complexes Ln–L in this work is less than that of complex $Zn_2(L2O)$, and large than that of complexes Zn(L1OH). The fact that the true second-order rate constants and deprotonation constant of coordination water of complexes $GaL2H_{-1}$, GaL2 designed and synthesized in this work are $0.0927\ mol^{-1}\ dm^3\ s^{-1}$, $0.000101\ mol^{-1}\ dm^3\ s^{-1}$ and 7.73 can sufficiently indicate that the complex Ga-L2 designed and synthesized in this work is excellent mononuclear catalyst of hydrolysis of HPNP at physiological condition (pH 6.721–8.318, pK_a = 7.73).

3.4. The influencing factors

From the data in Table 3, it is shown for the hydrolysis rate constants of complexes LnL and $LnLH_{-1}$, L1 < L2, so we think the steric hindrance is a very important influencing factor. The substitute group of L1 is bulky rigid benzyl group, and that of L2 is isobutyl. The bigger steric hindrance of L1 makes the coordination of complexes LnL and $LnLH_{-1}$ with substrate harder that counteract the catalysis of complexes to hydrolysis of HPNP.

And meanwhile, for the ligands L1, L2, the complexes of Gd(III) has better catalysis effect than the complexes of La(III). Due to Gd(III), La(III) have the same electron charge, but Gd(III) has the smaller radius and has the larger electron density, therefore, coordinated water on Gd(III) is easier to deprotonate to form hydroxyl group, OH^-, than corresponding La(III) complexes. We can draw conclusion that the catalysis rate of the complexes of Gd(III) is bigger than that of the La(III) complexes.

Acknowledgment

This project was supported by the National Natural Science Foundation of China (20371028).

References

[1] Y. Pocher, J.T. Stone, Biochemistry 7 (1968) 2936–2945.
[2] L.N. Ji, T.H. Mo, Introduction to Bioinorganic Chemistry, 2nd ed., Zhongshan University publishing, Guangzhou of China, 2001, pp. 1–7.
[3] O. Iranzo, A.Y. Kovaleveky, J.R. Morow, J.P. Richard, J. Am. Chem. Soc. 125 (2003) 1988–1993.
[4] L. Bincheng, L. Weimin, Huaxueshji 5127 (1983) 109–1011.
[5] D.A. Brown, D.A. Usher, J. Chem. Soc. 87 (1965) 6558–6564.
[6] H.K. Lin, Q. Liu, H. Lin, Trans. Metal Chem. 31 (2006) 325–332.
[7] S.P. Sinha, Helv. Chim. Acta 58 (1975) 1978.
[8] H.W. Sun, PhD Thesis, Nankai University, 1997, pp. 145.
[9] A.D. Zuberbuhlen, T.A. Kaden, Talanta 29 (1982) 201.
[10] D.H. Vance, A.W. Czarnik, J. Am. Chem. Soc. 115 (1993) 12165.
[11] W.P. Jencks, Catalysis in Chemistry and Enzumology, Dover Publications, New York, 1987 (Chapter 3).
[12] R. Wolfenden, M.J. Snider, Acc. Chem. Res. 34 (2001) 938–945.