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Journal of Molecular Catalysis A: Chemical 263 (2007) 70–76
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Kinetics and mechanism of promoted hydrolysis of 2-hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) by complexes of RPAla and RPVal with La(III), Gd(III)

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Received 14 February 2006; accepted 15 May 2006
Available online 27 September 2006

Abstract

Two multidentate ligands: *N*,*N*′-di-(propionic acid-2′-yl-)-2,9-di-aminomethylphenanthroline (L1) and *N*,*N*′-di-(3′-methylbutyric acid-2′-yl-)-2,9-di-aminomethylphenanthroline (L2) were synthesized. The hydrolytic kinetics of 2-hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) catalyzed by complexes of L1 and L2 with La(III), Gd(III) have been studied. Both LnL and $LnLH_{-1}$ have been examined as catalysis for the hydrolysis of HPNP in aqueous solution at 298 K, $I = 0.10\,mol\,dm^{-3}$ KNO_3 at pH range 7.4–9.1, respectively. Kinetic studies show that both LnL and $LnLH_{-1}$ have activity, but $LnLH_{-1}$ is more active than LnL in the hydrolysis reaction of HPNP. The second-order rate constants of hydrolysis of HPNP are $k_{GdL1H_{-1}} = 0.0466\,mol^{-1}\,dm^3\,s^{-1}$, $k_{GdL1} = 0.000037\,mol^{-1}\,dm^3\,s^{-1}$ for $GdL1H_{-1}$ and GdL1, respectively. New mechanism was proposed for the hydrolysis reaction of HPNP catalyzed by LnL and $LnLH_{-1}$.

Keywords: Hydrolysis; 2-Hydroxypropyl-*p*-nitrophenyl phosphate (HPNP); Kinetics; Mechanism

1. Introduction

In recent years, lot of studies showed that many transition metal complexes, espectively dinuclear zinc(II) complex mimic hydrolase, can dissociate the bond of phosphate more effectually as catalysts [1]. But because rare earth metal ions have high charges, high numbers of coordinate bonds and incompact room than commen transition metal ions such as Cu(II), Zn(II), thus, various types of Ln(III) complexes have been designed to investigate or mimic the functions of bio-enzymes [2]. In this paper, we report the hydrolytic kinetics of 2-hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) catalyzed by complexes of *N*,*N*′-di-(propionic acid-2′-yl-)-2,9-di-aminomethylphenanthroline (RPAla, L1) and *N*,*N*′-di-(3′-methylbutyric acid-2′-yl-)-2,9-di-aminomethylphenanthroline (RPVal, L2) with La(III), Gd(III) and new mechanism for the hydrolysis reaction of HPNP catalyzed by LnL and $LnLH_{-1}$. Our interest was to understand functions of metal ions in biological hydrolysis process.

2. Experimental section

2.1. Materials

All solvents used were of analytical grade and were purified by standard technique prior to use unless otherwise noted. All aqueous solution were freshly prepared using redistilled water. Other chemicals used were of analytical reagent of high purity grade. 2-Hydroxypropyl-*p*-nitrophenyl phosphate (HPNP) was prepared as literatures [3,4]. *N*,*N*′-di-(propionic acid-2′-yl)-2,9-di-aminomethylphenanthroline (RPAla, L1) and *N*,*N*′-di-(3′-methylbutyric acid-2′-yl-)-2,9-di-aminomethylphenanthroline (RPVal, L2) were prepared as Fig. 1.

RCH (NH_2) COOH (10 mmol) (L_1: R = CH_3; L_2: R = $(CH_3)_2CH$) and NaOH (10 mmol) were suspended in distilled H_2O (20 ml), and 2,9-dicarboxaldehyde-1,10-phenanthroline (5 mmol) was added to the solution slowly with stirring at room temperature. Then $NaBH_4$ (2.0 g) was

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doi:10.1016/j.molcata.2006.05.057

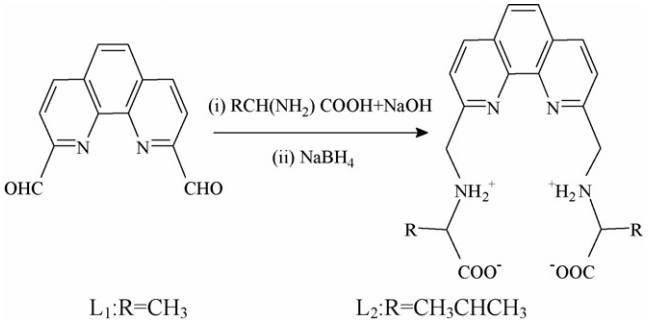

Fig. 1. Synthesis route of the ligands.

added slowly as reducer in an ice-water bath. After adding a suitable volume of concentrated HCl, the white precipitate was collected, washed with EtOH recrystallized from EtOH–H_2O, and dried in a vacuum desiccator. L_1 yield: 44%. ^{1}H NMR (D_2O, δ ppm): 7.79, 8.46, 7.88 (d, d, s, 6H, phen); 4.61 (q, 4H, –CH_2–); 1.62, 4.00 (d, q, 6H, 2H, $CH_3CH<$). Elemental analysis: for $C_{20}H_{22}N_4O_4{\cdot}3.5H_2O$, % found (% cacld.) C: 54.1 (53.9); H 6.5 (6.5); N 12.8 (12.6). L_2 yield: 40%. ^{1}H NMR (D_2O, δ ppm): 7.53, 8.16, 7.63 (d, d, s, 6H, phen); 4.10 (q, 4H, –CH_2–); 0.96, 2.99, 1.93 (d, d, d, 12H, 2H, 2H, $(CH_3)_2CHCH<$). Elemental analysis: for $C_{24}H_{30}N_4O_4$–$4H_2O$, % found (% cacld.) C: 56.4 (56.5); H: 7.5 (7.5); N: 10.9 (10.9).

2.2. Potentiometric determination

Potentiometric determination was measured in a 50 ml jacketed cell thermostated at 298.2 ± 0.1 K by a refrigerated circulating water bath. Anaerobic conditions 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 [5]. 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 [6] based on the improved TITFIT technique [7]. The final results were the averages of three independent titrations, each titration containing about 70 experimental points.

2.3. Kinetic study of hydrolysis of HPNP

A kinetic study was carried out by the UV spectral method using a Beckman DU-8B spectrophotometer. The hydrolysis rate of HPNP in aqueous solution was measured by an initial slope method following the increase in 400 nm absorption of the released *p*-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.

Table 1
The potentiometric constants of the ligands L_1 and L_2 at 298.2 ± 0.1 K

Ligands	log K_1	log K_2	log K_3
L_1	9.59	8.47	7.27
L_2	9.68	8.53	7.75

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), which were linear for at least three reaction halftimes. All the experiments were run 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 indicates that the complexes formed by La(III) and Gd(III) with L1 and L2 are performed at 1:1 metal–ligand molar ratios, respectively. The stability constants of $LnLH_m$ ($m = 2 \sim -1$) complexes in the 1:1 ratio are shown in Table 2. From the species percentage distribution diagrams of the Ln–L binary system (see Fig. 2) it is find that the mode $LnLH_{-1}$ (1 1 −1) is formed in the solution when pH > 7.5.

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 5. LnL (1 1 0) can release a proton and transfer to $LnLH_{-1}$ at pH > 7.5 which is a good nucleophilic metal-bond hydroxide specie and they can be used as enzyme models for catalyzing the hydrolysis of phosphate diesters because of their nucleophilic group OH^-.

3.2. Molar extinction coefficient of NP^-

The kinetic study of hydrolysis of HPNP was carried out by monitoring the amount of *p*-nitrophenolate ion (NP^-) produced in solution at 400 nm. The use of buffer for the analysis was

Table 2
The stability constants of binary complexes of the ligands L_1 and L_2 with respective La(III), Gd(III) at $I = 0.1$ mol dm^{-3} KNO_3, 25 ± 0.1 °C

Metal	Constants	L_1	L_2
La	log β_{112}	29.08 ± 0.11	26.16 ± 0.24
	log β_{111}	22.51 ± 0.16	19.08 ± 0.35
	log β_{110}	15.81 ± 0.33	9.99 ± 0.37
	log β_{111}	6.23 ± 0.22	0.75 ± 0.04
Gd	log β_{112}	32.22 ± 0.15	27.01 ± 0.24
	log β_{111}	25.73 ± 0.20	22.88 ± 0.51
	log β_{110}	19.86 ± 0.42	14.79 ± 0.33
	log β_{111}	10.63 ± 0.71	5.90 ± 0.76

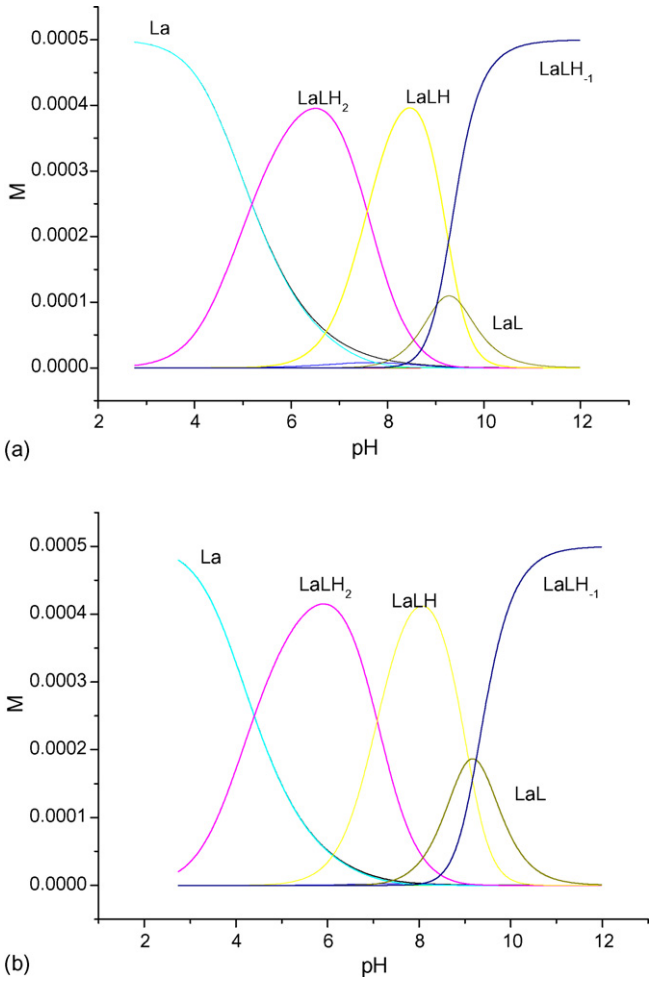

Fig. 2. Percent distribution diagrams for species formed in: (a) La(III)–L1 and (b) La(III)–L2 system as a function of pH.

required since the change of pH values of the reaction solution would cause change in the concentration of the NP^-. To determine the rate constant one should know the molar extinction coefficient of NP^-, which varies considerably with pH values of the reaction solution. In solution *p*-nitrophenol dissociate as follow:

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

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

According to Beer's law:

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

where ε_{obs} is the observed molar extinction coefficient of HNP, ε_{NP} the molar extinction coefficient of the NP^- anion, b the cell length, and A is the absorption of the samples. From Eqs. (2) and (3) is obtained:

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

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

Table 3
k_{obs} ($\times 10^{-5}$ s^{-1}) values of HPNP hydrolysis catalyzed by GdL_1 and GdL_1H_{-1} (298 K, I = 0.1 mol dm^{-3} KNO_3, 0.02 mol dm^{-3} tris)

10^{-4} $C_{GdRPAla}$ (mol dm^{-3})	pH					
	7.477	7.830	8.071	8.356	8.688	9.092
2.0	9.662	11.485	14.543	20.460	30.285	49.892
3.0	14.056	17.369	21.921	30.542	46.634	73.593
4.0	18.563	23.898	29.077	40.631	61.469	98.845
5.0	23.988	29.146	36.882	50.498	77.254	122.55

With the plot of $1/\varepsilon_{obs}$ versus $[H^+]$ according to Eq. (5), the molar extinction coefficient ε_{NP} and the dissociation constant of *p*-nitrophenolate K_a at 400 nm in 0.020 mol dm^{-3} Good's buffers were obtained with the values of 17,900 mol^{-1} dm^3 cm^{-1} and 7.66×10^{-8} mol dm^{-3}, respectively, which is consistent with the reported value [8].

3.3. Kinetic studies of hydrolysis of HPNP

Under used experimental conditions, the hydrolysis rate increases linearly with the increase of concentration of [HPNP]. Thus, the hydrolysis is first-order with respect to [HPNP]. The rate v can be written as follow form:

$$v = \frac{dc_{HPNP}}{dt} = \frac{dA}{\varepsilon_{obs} b\, dt} = k_{obs}[HPNP] \quad (6)$$

With the plots of v versus [HPNP], the pH-dependent observed first-order rate constants k_{obs} are obtained over the 7.4–9.1 pH range for the 1:1 complexes, respectively. For example, the k_{obs} of hydrolysis of HPNP catalyzed by GdL_1 and GdL_1H_{-1} are shown in Table 3.

Where v is the hydrolysis rate and k_{obs} is the observed rate constant. The hydrolysis of HPNP is a combination of three factors: (1) k_{cat}^{obs} is the catalysis by metal complexes, (2) k_{OH} is the catalysis by OH^- and (3) k_0 is the effect of solvent, so v should be represented by Eq. (7):

$$v = k_{obs}[HPNP] = (k_{cat}^{obs}[Ln\text{–}L]^T + k_{OH}[OH^-] + k_0)[HPNP] \quad (7)$$

where $[Ln\text{–}L]^T$ is the total concentration of metal complexes Ln–L. 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 Ln–L, k_{cat}^{obs} can be gotten. The apparent hydrolysis rate constants, k_{cat}^{obs} at different pH values were shown in Table 4. As discussed earlier, there are two types of nucleophile in the 1:1 system: LnL and $LnLH_{-1}$, with the equilibrium constant K_a^2. The concentration of LnL and $LnLH_1$ can be represented by Eqs. (8) and (9):

$$[LnL] = \frac{[Ln\text{–}L]^T[H^+]}{K_a^2 + [H^+]} \quad (8)$$

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

Table 4
The apparent rate constants catalyzed hydrolysis of HPNP by Ln–L complexes, k_{cat}^{obs} (mol^{-1} dm^3 s^{-1}), at different pH values

pH	$[H^+]$ ($\times 10^{-8}$ mol dm^{-3})	k_{cat}^{obs} (mol^{-1} dm^3 s^{-1})			
		Gd(III)L_2	Gd(III)L_1	La(III)L_2	La(III)L_1
7.477	4.041	0.00426	0.00467	0.00235	0.00257
7.830	1.793	0.00561	0.00582	0.00277	0.00313
8.071	1.029	0.00726	0.00727	0.00330	0.00385
8.356	0.534	0.01037	0.01008	0.00435	0.00528
8.688	0.249	0.01586	0.01541	0.00645	0.00815
9.092	0.098	0.02433	0.02462	0.01037	0.01365

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

$$k_{cat}^{obs}[\text{Ln–L}]^T = k_{LnL}[\text{LnL}] + k_{LnLH_{-1}}[\text{LnLH}_{-1}] \quad (10)$$

where k_{LnL} and $k_{LnLH_{-1}}$ stand for the second-order hydrolysis rates constants of HPNP catalyzed by LnL and $LnLH_{-1}$, respectively.

Eq. (11) could be obtained from Eqs. (8)–(10):

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

The apparent hydrolysis rate constants of complexes Ln–L, k_{cat}^{obs}, increase with the increase of pH values of reaction solution. When the total apparent hydrolysis rate constant catalyzed by the complexes Ln–L, k_{cat}^{obs}, is plotted against pH values, resulting curve indicate the characteristics of kinetic process controlled by acid-base equilibrium (duo to a deprotonation of the coordination water on the complex LnL) (seen Fig. 3). This phenomenon is same with one reported Richard [9]. It is interesting that ionization of complexes LnL at basic pH is due to loss of a proton from a water bound on Ln(III), because the pH-rate profiles show that the ionization state of this water is critical for catalytic activity.

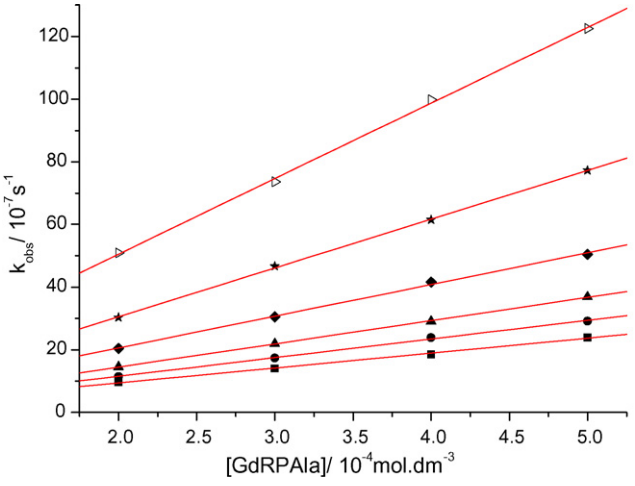

Fig. 3. Plots of k_{obs} vs. $[\text{GdRPAla}]^T$. The pH from bottom to up is 7.477, 7.830, 8.071, 8.356, 8.688 and 9.092, respectively.

The pH-rate profiles of the second-order rate constants k_{cat}^{obs} for the transesterification of HPNP catalyzed by complexes Ln–L provide the following important insights into the catalytic reaction mechanism.

There is a downward break in the pH-rate profile for the hydrolysis of HPNP catalyzed by Ln–L complex system that is centered at the pK^2 for deprotonation of a bound water molecule to form the monohydroxy complex $LnLH_{-1}$.These pH-rate profiles show that the complex LnL is less active species catalyzed hydrolysis of HPNP than $LnLH_{-1}$ and is converted to a more active species $LnLH_{-1}$ upon loss of a proton. Jencks [10] considered that a kinetics provides no information about whether this proton is from catalyst or substrate. However, Wolfenden [11] 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 function in some way to facilitate ionization of this hydroxyl. Richard [9] 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 catalysts Zn_2(L2O)(OH) or Zn(L1OH)(OH) may occur as a pre-equilibrium step to form the protonated catalysts Zn_2(L2O)(H_2O) and Zn(L1OH)(H_2O), respectively, and the C2-oxyanion of substrate which would then undergo nucleophile addition to the phosphate diester.

We consider that the lost proton correlated with a downward break in the pH-rate profile come from the water molecule coordinated on Ln(III) of the complex LnL, because pK_a of free water at 298 K is about 14 and pK_a of isopropyl alcohol at 298 K is about 16. When water molecule coordinated with Ln(III) of complex LnL, at action of Ln(III) of complex LnL the pK_a of coordinated water markedly decrease and that pK_a of 2-hydroxypropyl of substrate still is 16. The lost proton coming from water molecule coordinated on Ln(III) of complex LnL caused a downward break in the pH-rate profile. A losting proton complex LnL was changed to complex $LnLH_{-1}$ and the hydroxyl group of the complex $LnLH_{-1}$ attack the 2-hydroxypropyl of substrate. The proton of 2-hydroxypropyl transfer to the hydroxyl group of complex $LnLH_{-1}$ with intramolecular attack of C2-oxygen to the phosphate diester immediately. This transferring proton can not caused a change of pH value of the reaction solution, and that water molecule coordinated on Ln(III) of complex LnL directly attacked the P atom of substrate HPNP, this result also lead the *p*-nitrophenate ion leave from HPNP. Because the electron cloud density on C2-oxyanion of substrate HPNP is large much than one on oxygen atom of water molecule coordinated on Ln(III) of complex LnL, therefore, the activity catalyzed hydrolysis of HPNP for complex $LnLH_{-1}$ is higher than one for complex LnL, i.e. $k_{LnLH_{-1}}$ is large much than k_{LnL}. The concentration of complex $LnLH_{-1}$ increase with the increase of pH value of reaction solution, therefore, the second-order

Table 5
The second-order rate constants k_{LnL}, $k_{LnLH_{-1}}$ and the deprotonation dissociation of LnL (pK_a^2) in the hydrolysis of HPNP

Complexes	k_{LnL} (mol^{-1} dm^3 s^{-1})	$k_{LnLH_{-1}}$ (mol^{-1} dm^3 s^{-1})	pK_a^2 (calculation)	pK_a^2 (titration)
$Gd(III)L_2$	0.0031	0.0405	8.89	8.92
$Gd(III)L_1$	0.0037	0.0466	9.23	9.07
$La(III)L_2$	0.0020	0.0217	9.24	9.10
$La(III)L_1$	0.0021	0.0304	9.58	9.12

rate constants, k_{cat}^{obs}, increase with the increase of pH value of reaction solution. 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) and list in Table 5. From Table 5 it could be found that deprotonation 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. This is powerful evidence of out viewpoint.

Based on the results mentioned above, the catalytic mechanism for the 1:1 Ln–L systems is proposed as shown in Fig. 4 [12,13]. The hydrolysis process involves as following steps: (1) the water molecule coordinated on Ln(III) of complex LnL released proton H^+ transfer to hydroxyl group at action of Ln(III) of complex LnL, therefore, there exists a dissociation equilibrium of the water molecule coordinated on Ln(III) of complex LnL, exist two species: $LnLH_{-1}$ and LnL in reaction solution; (2) the initial interactions of O^-, oxyanion on P atom of HPNP with the central Ln(III) of complexes $LnLH_{-1}$ and LnL, respectively; (3) the hydroxyl group coordinated on Ln(III) of complex $LnLH_{-1}$ attacked the C2-hydroxyl of HPNP, H^+ of C2-hydroxyl of HPNP transfer to the hydroxyl group coordinated on Ln(III) of complex $LnLH_{-1}$ and the hydroxyl group transfer to water molecule, then C2-oxyanion of substance HPNP undergo intramolecular attack to the phosphate diester, the lactone was formed and the *p*-nitrophenolate was released for complex $LnLH_{-1}$, and that the water molecule coordinated on Ln(III) of complex LnL direct attack the P atom of substrate HPNP, and *p*-nitrophenolate ion was released for complex LnL; (4) then the lactone of phosphonic acid was released at an attack of a water molecule and a catalytic cycle is completed for complex $LnLH_{-1}$ and that the 2-hydroxypropyl phosphate ion also was released at an attack of a water molecule and a catalytic cycle is completed for complex LnL (Fig. 5).

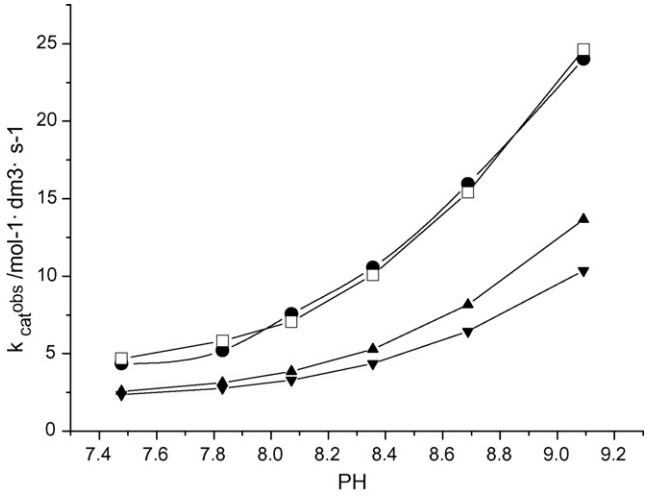

Fig. 4. The curve of relation of apparent rate constants of hydrolysis of HPNP catalyzed by complexes LnL, k_{cat}^{obs} vs. pH: (■) GdL_2, (●) GdL_1, (▲) LaL_1 and (▼) LaL_2.

From the data in Table 5, we find that as catalyst the efficiency of complex $LnLH_{-1}$ is more higher than LnL. Because the electron cloud density on C2-oxygen anion of HPNP is large much than one on oxygen atom of H_2O coordinated on complex LnL, therefore, the rate constant of hydrolysis of HPNP of complex $LnLH_{-1}$, $k_{LnLH_{-1}}$, is large much than one of complex LnL, k_{LnL}.

In the paper of Richard [9] second-order rate constants k_{Zn} (mol^{-1} dm^3 s^{-1}) for the catalyzed reactions were determined as the slope of linear plots of k_{obsd} against catalyst concentration, but only obtained apparent second-order rate constants $k_{Zn} = 0.25\ mol^{-1}\ dm^3\ s^{-1}$ for complex $Zn_2(L2O)$ and $k_{Zn} = 0.0013\ mol^{-1}\ dm^3\ s^{-1}$ for complex Zn(L1OH) at pH = 7.6 and do not obtained true second-order rate constant of complex $Zn_2(L2O)(OH)$, $Zn_2(L2O)(H_2O)$ and Zn(L1OH)(OH), $Zn(L1OH)(H_2O)$, respectively, furthermore, the second-order rate constant k_{Zn} increase with the increase of pH value of reaction solution .If by means of non-linear least-squares fit of k_{Zn} versus [H^+], the true second-order rate constants $k_{Zn_2(L2O)(OH)}$, $k_{Zn_2(L2O)(H_2O)}$ and $k_{Zn(L1OH)(OH)}$, $k_{Zn(L1OH)(H_2O)}$ can be obtained according to Eq. (11), respectively.

From the data in Table 5, it is found for second-order rate constants of hydrolysis of HPNP catalyzed by complexes $LnLH_{-1}$ and LnL1, L1 > L2. This is due to isopropyl with stronger steric effect than methyl can weaken the coordination capability and the stability of complexes, meanwhile also can weaken the catalysis capability of complexes to hydrolysis of HPNP.

From the data in Table 5, it could also be found that the second-order rate constant of Gd(III) are greater than the same complexes of La(III). This is due to Gd(III) with more smaller ionic radius than La(III) which have higher charge density and can combine more tightly with coordination water, therefore, coordination water easier loss proton and change to OH^-. From the data in Table 5 it could also found that the deprotonation constants of water coordinated on complexes Gd(III), pK_a^2 values, were smaller than La(III). Meanwhile Gd(III) can combine more tightly with HPNP, therefore, it is more favorable to transition of electron of HPNP and distort of ester bond than La(III).

We obtained the second-order rate constants of hydroltsis of HPNP, $k_{GaL1H_{-1}} = 0.0466\ mol^{-1}\ dm^3\ s^{-1}$, $k_{GaL1} = 0.000037\ mol^{-1}\ dm^3\ s^{-1}$ for GaRPAla complex system and deprotonation constant of H_2O coordinated on complex GaRPAla, $pK_a^2 = 9.23$, Therefore, the complexes GaRPAla designed and synthesized by us is very excellent mononuclear catalyst and can effectively catalyze the hydrolysis of HPNP.

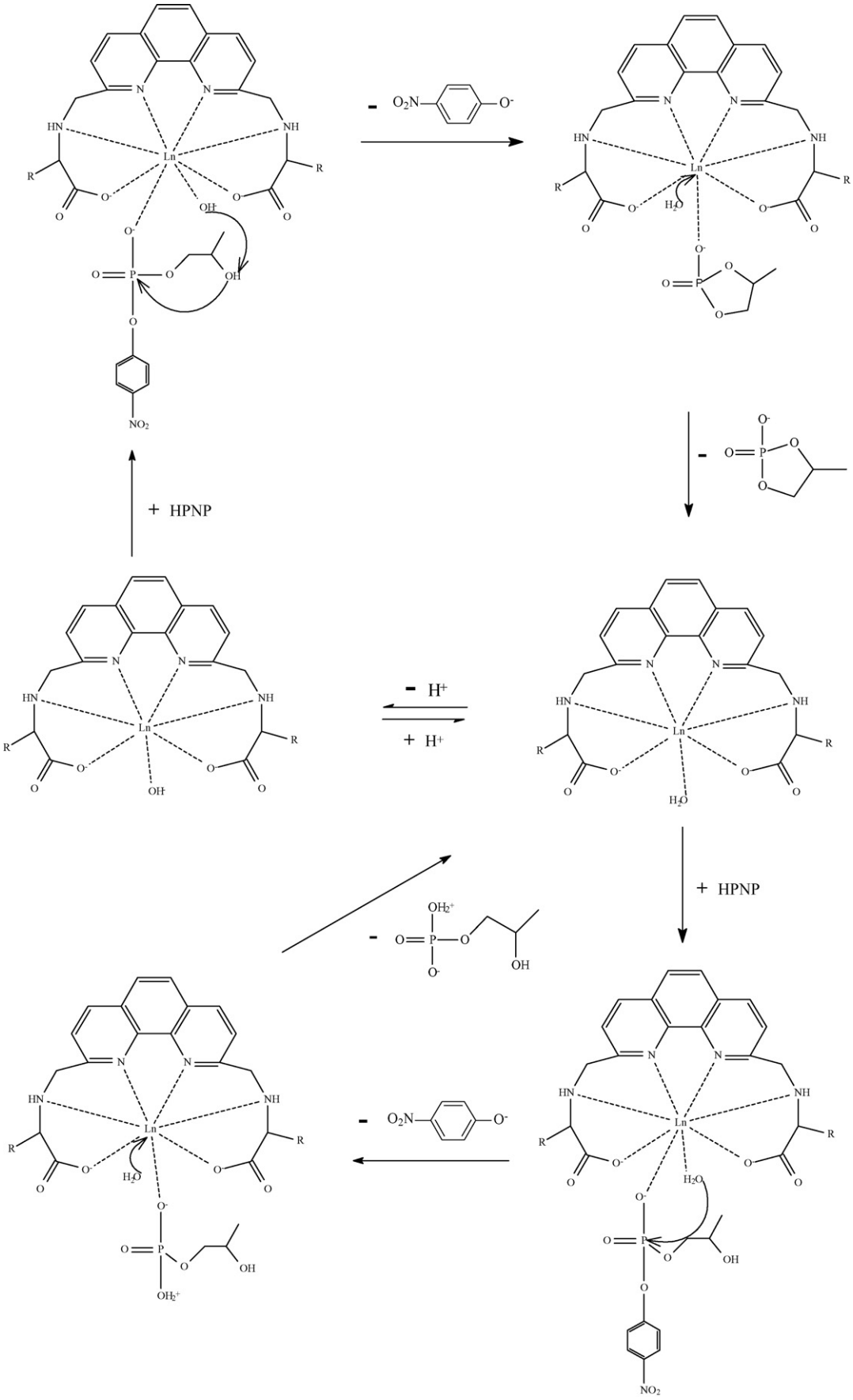

Fig. 5. The proposed mechanism of the hydrolysis of HPNP catalyzed by Ln–L.

4. Conclusion

In summery, the results studied in this paper provide the evidence for the importance of rare earth metal ion to the capability catalyzed hydrolysis of HPNP for complexes by comparison of rate constants and by establishing the mechanism of the 1:1 catalysts. The highly efficient catalysis of complexes reported in this paper may provide a clue for the design of the hydrolytic enzyme through the combination of different kinds of ligands and metal ions. One can change Zn(II) metal ion to rare earth metal ion having higher charge, higher number of coordination bond and compact room in a homogeneous fashion to achieve faster reaction rate. Work in this area is underway.

Acknowledgments

This project, was supported by the National Natural Science Founding of China (20371028) and Natural Science Founding of Tianjin (023605811).

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