



Interaction of Naphthalene Anhydride Derivative with Adenosine Triphosphate and the Catalytic Influence on Adenosine Triphosphate Hydrolysis

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Received: 23 January 2014;

Accepted: 8 May 2014;

Published online: 26 December 2014;

AJC-16551

A new compound, 1,8-naphthalene diformate-L-histidine (L) was synthesized and characterized by elemental analysis, ^1H NMR and ^{13}C NMR. The interaction between 1,8-naphthalene diformate-L-histidine and adenosine triphosphate (ATP) has been studied by fluorescence titration experiment. The stability constant between 1,8-naphthalene diformate-L-histidine and ATP is $6.72 \times 10^5 \text{ L mol}^{-1}$. Furthermore, the catalysis of ligand (L) on ATP hydrolysis was also studied by molybdenum blue method. The optimum temperature is 40°C and pH value is 4. The hydrolysis rate constant (K_{obs}) is 0.1218 h^{-1} when 1,8-naphthalene diformate-L-histidine is added. It is increased about 11.7 times comparing with the hydrolysis rate constants of ATP without the addition of 1,8-naphthalene diformate-L-histidine, $1.1041 \times 10^{-2} \text{ h}^{-1}$, in the same condition. A reasonable mechanism that occurs through an addition-elimination is proposed. These data provide a new role of 1,8-naphthalene diformate-L-histidine as a novel catalyst for ATP hydrolysis.

Keywords: Adenosine triphosphate, L-histidine, Imidazole ring, Catalytic hydrolysis.

INTRODUCTION

Adenosine triphosphate (ATP) is one of the most important substances of human and animal body tissues, it is a phosphate compound with high-energy¹⁻⁴. It is not only the main energy storage material of organisms, but also the main source of energy in the process of life. In addition, it plays an important part in the storage and conversion of energy during the process of ATP hydrolysis⁵. The hydrolysis of ATP is dependent on the efficient catalysis of ATPase enzyme. According to the complex of the organic system, the simulation research of mimic enzyme for ATP hydrolysis attracted researchers' great attention⁶. Current interest mainly focuses on the molecular recognition and catalysis hydrolysis of nucleotides by the polyamine ligands and phenanthroline as well as polyoxomolybdates^{7,8}. Amino acids play central function both as building blocks of protein and as intermediates in metabolism⁹. It is important to study amino acid structure and property for understanding protein structure and property.

Ma *et al.*¹⁰⁻¹² have studied the selective weak interaction between $N\alpha$ -4-tosyl-L-arginine methyl ester hydrochloride (TAME) and adenosine-5'-triphosphate (ATP) through fluorescence spectrophotometry, Fourier transform infrared spectroscopy and ^{31}P NMR methods. It has been identified by

fluorescence titration experiments that TAME exhibited high selectivity to ATP over ADP and AMP. These experimental results indicated that the interaction sites were the guanidinium group of TAME main-chain and the γ -phosphate group of ATP and the interaction took place through hydrogen bond and electrostatic force.

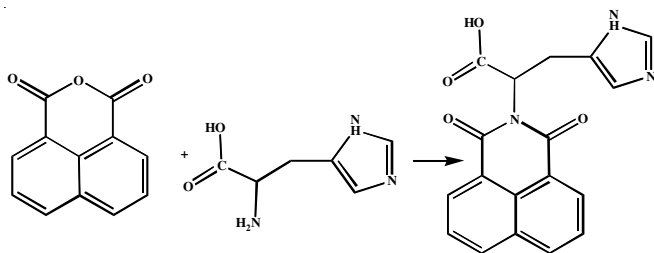
Among the amino acids, L-histidine is one of the strongest metal-coordinating ligands and plays an important role in the binding of metal ions by proteins¹³. L-Histidine has amino, imidazole and carboxylate groups as three potential binding sites^{14,15}. In addition, it also plays an important part in enzyme catalysis and metalloproteins¹⁶. In the complexes of mimic enzyme, the local structure, dynamics variation and biological function could usually be resulted from the interactions between histidine and adenosine group of ATP¹⁴.

In this paper, an L-histidine derivative bearing an an-naphthalene unit was synthesized¹⁷. The interaction between the ligand and ATP has been proved that there has superinteraction between them and the bonding contact is $6.72 \times 10^5 \text{ L/mol}$. The results of catalytic hydrolysis in the ATP-ligand binary system have been studied by molybdenum blue method. The catalytic effect can attained 10 times. Furthermore, a reasonable mechanism that occurs through an addition-elimination is proposed.

EXPERIMENTAL

1,8-Naphthalene anhydride, adenosine 5'-triphosphate disodium salt (ATP) and histidine were all purchased from J&K. Ammonium molybdate and ascorbic acid were purchased from Tianjin Chemical Reagent Factory. DMSO and KOH were both purchased from Tianjin Guangfu Fine Chemical Research Institute. All reagents used were of analytical grade.

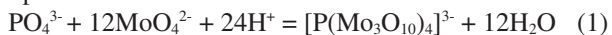
Synthetic process of 1,8-naphthalene diformate-L-histidine (L): 1,8-Naphthalic anhydride (1.50 g, 7.57 mmol) was suspended in 40 mL of DMSO and heated to 100 °C in a reflux apparatus. Histidine (2.4852 g, 16 mmol) was dissolved in 2 mL of 8 mol/L KOH solution and added dropwise to the suspension. The mixture was stirred at 150 °C for 3 h and then cooled to room temperature. The residue was collected by filtration and washed twice with a mixture of DMSO/water (2:1) solution. To remove DMSO, the residue was dissolved in a minimum amount of hot water and precipitated by the addition of acetone. The solid material was then collected by filtration, washed twice with acidic acetone and dried under vacuum to afford 1.9 g (75 % yield) of the desired product (**Scheme-I**). ¹H NMR (400 MHz, D₂O) δ: 8.11 (2H, d), 7.65 (2H, s), 7.52 (1H, s), 7.31 (2H, t), 6.71 (1H, s), 5.75 (1H, dd), 3.49 (2H, d).



Scheme-I: Synthetic process of 1,8-naphthalene diformate-L-histidine (L)

Fluorescence detection: Fluorescence spectra of the recognition between 1,8-naphthalene diformate-L-histidine and ATP were recorded on a F-2500 spectrometer (Hitach, Japan) with a slit width of 10 nm using a 10 mm path quartz cell. The fluorescence intensity was measured at wavelengths $\lambda_{\text{ex}}/\lambda_{\text{em}} = 250/510$ nm. The pH of the solutions was adjusted by hydrochloric acid or sodium hydroxide solutions and measured on a PHB-3 pH meter (Shanghai San-Xin Instrumentation, Inc).

Molybdenum blue method: The optimum temperature and pH values of ATP aqueous solutions catalyzed by 1,8-naphthalene diformate-L-histidine were determined by molybdenum blue method in water bath for 2 h at 30 °C. The principle of this method is:



Concentration of orthophosphate anion (Pi) resulting from ATP hydrolysis was measured by a spectrophotometric test in HP 8453 of VG Scitntific. Briefly, in hydrochloric acid solution, orthophosphate ions react with molybdate ions to form molybdo-phosphoric acid. Ascorbic acid reduces it into phosphomolybdenum blue that is determined spectrophotometrically at the appropriate wavelength. The pH value of the solution was recorded at room temperature with a PHB-3 pH meter and adjusted to the desired pH using 1.2 mol L⁻¹ NaOH or HCl.

10 mL mixed colour reagent was prepared freshly for use by mixing the following stock solutions: (1) 2 mL of 15 g L⁻¹ ammonium molybdate tetrahydrate solution; (2) 1 mL of 25 g L⁻¹ ascorbic acid solution; (3) 1 mL reactive liquid including 2×10^{-4} mol L⁻¹ ATP and 1,8-naphthalene diformate-L-histidine were taken at intervals 10 min or some time. Then the mixture was diluted to 10 mL with ultra-pure water and mixed well. The reaction endpoint was reached in most cases about 10 h.

RESULTS AND DISCUSSION

pH-Dependence of the fluorescence intensity: The changes of fluorescence intensity at the maximum emission wavelength (256 nm) of systems (L and L+ATP with pH values in aqueous solutions) are shown in Fig. 1. Under weak acidic or alkaline conditions (pH 5-12), the fluorescence intensity of 1,8-naphthalene diformate-L-histidine is very weak and then has a sharp increase when the pH decreases to 5.

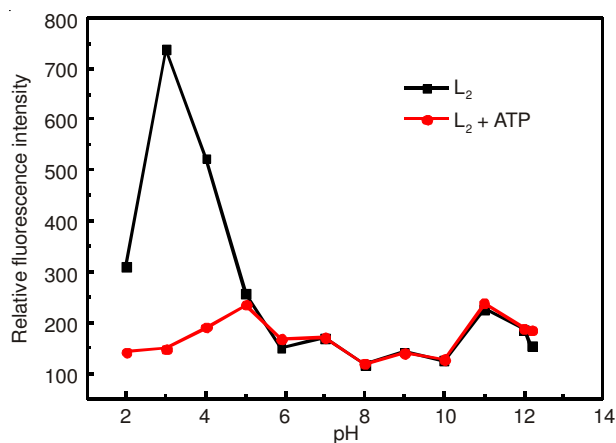


Fig. 1. Effect of pH on fluorescence intensity of L and L+ATP systems. (L = 2×10^{-6} mol/L, ATP = 2×10^{-4} mol/L, L:ATP = 1:1)

This fluorescence enhancement behaviour is due to the inhibition of the photoinduced electron transfer (PET) processes from the amine nitrogen atom to the naphthyl group by the protonation of the amine group of 1,8-naphthalene diformate-L-histidine, which is responsible for the fluorescence quenching¹⁸. However, a decrease in fluorescence intensity is observed under strongly acidic conditions pH 1. This is probably due to the protonation of the imidazole nitrogen of 1,8-naphthalene diformate-L-histidine under strong acid conditions, which may causes an electron-transfer process from the excited naphthalenic unit to the electron-deficient imidazole part, inducing a decrease in emission intensity¹⁹.

The most interesting feature in this system is the quenching induced by the addition of ATP at pH values below 5. The obvious quenching can be observed at pH 3. This quenching effect might be ascribed to the PET or energy transfer from ATP to the photo-excited naphthalenic unit favored by hydrogen bonding and electrostatic interactions between 1,8-naphthalene diformate-L-histidine and the phosphate group and adenine fragment of ATP^{14,19}.

Chemical stoichiometry: Fig. 2 explains the fluorescence titration of 1,8-naphthalene diformate-L-histidine with ATP in aqueous solutions at pH 3. The intensity of the emission peaks decreased with the concentration increasing of ATP. It

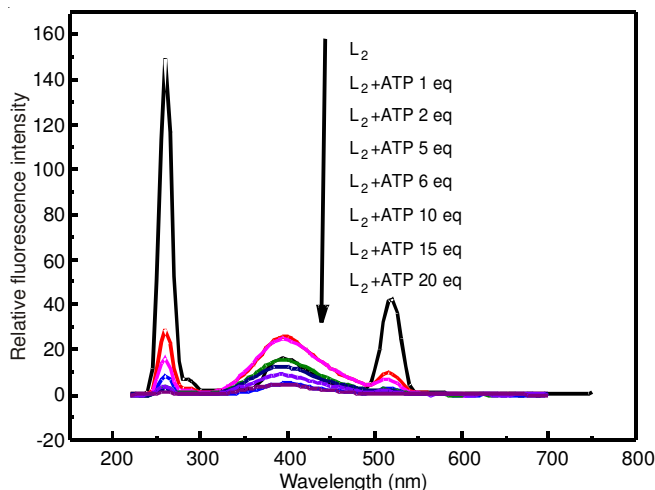
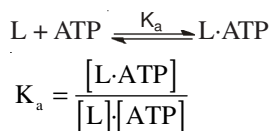


Fig. 2. Fluorescence spectra changes of L upon addition of ATP. ($L = 2 \times 10^{-6}$ mol/L, $ATP = 2 \times 10^{-4}$ mol/L, $pH = 3$)

is of great significance to the research of the interaction between 1,8-naphthalene diformate-L-histidine and ATP.

1,8-Naphthalene diformate-L-histidine and ATP can be assumed that they may form the complex of 1:1. Then the process of coordination can be showed as:



In the system, the concentration of ATP is much larger than the subject, so the stability constant of supramolecular system can be obtained according to the modified Benesi-Hildebrand equation:

$$\frac{1}{\Delta I_f} = \frac{1}{\alpha K_a [L]_0 [ATP]} + \frac{1}{\alpha [L]_0}$$

ΔI_f is the difference of the fluorescence intensity before and after the addition of ATP, α is the sensitive factor of the fluorescence intensity, $[I]_0$ is the initial concentration of 1,8-naphthalene diformate-L-histidine. Fig. 3 shows the plot of $1/\Delta I_f$ as a function of $1/ATP$. It's easy to find that the linear of the figure. Meanwhile, it strongly suggests formation of 1:1 complexes between 1,8-naphthalene diformate-L-histidine and ATP. We can also obtain the association constant $K_a = 6.72 \times 10^5$ L mol $^{-1}$. It further proved the formation of the stable complexes between 1,8-naphthalene diformate-L-histidine and ATP. It will be contributed to the further study of catalytic hydrolysis of ATP by 1,8-naphthalene diformate-L-histidine.

Catalytic hydrolysis of ATP by 1,8-naphthalene diformate-L-histidine: As shown in Fig. 4 the hydrolysis solution of ATP has the largest absorbance at 725 nm. The absorbance gradually increases along with reaction time, indicating that the concentration of inorganic phosphate is increased during the hydrolysis process of ATP. That is to say, the hydrolysis process of ATP has been performed with time going on.

Temperature effect on ATP hydrolysis: The temperature dependence of the ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine was studied in the temperature range from 30 to 80 °C using molybdenum blue method. As shown in Figs. 5 and 6, optimum temperature was found to be 40 °C.

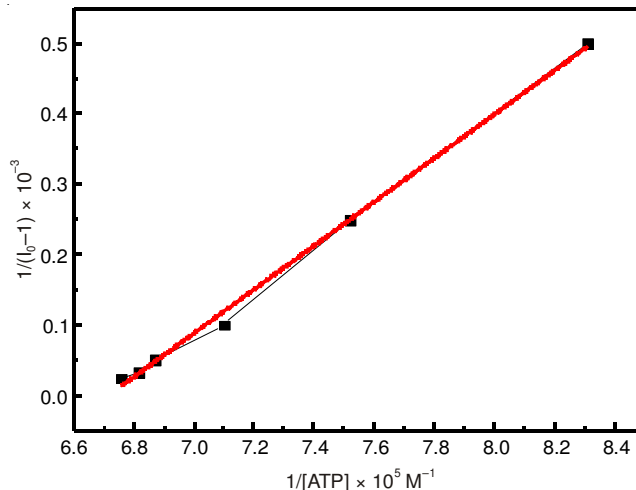


Fig. 3. Plot of $1/\Delta I_f$ as a function of $1/ATP$ (Benesi-Hildebrand plot)

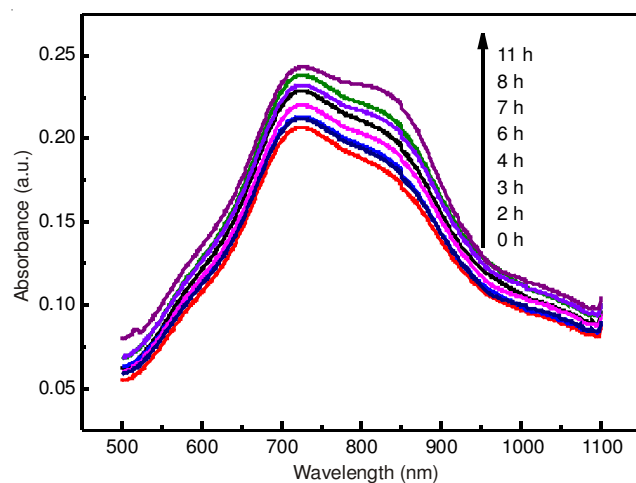


Fig. 4. UV-visible spectra of the molybdenum blue solutions in the different time of ATP hydrolysis. $T = 40$ °C, $pH = 5$, $L_1 = ATP = 2 \times 10^{-4}$ mol/L

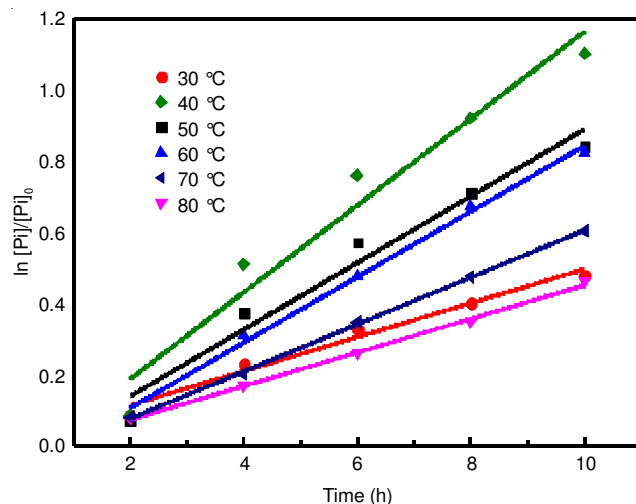


Fig. 5. Plot of $\ln ([Pi]/[Pi]_0)$ as a function of time in different temperature: $pH = 4$, $L_1 = ATP = 2 \times 10^{-4}$ mol/L

As is shown below, the values of the rate constant (K_{obs}) of ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine were calculated by the plot of $\ln ([Pi]/[Pi]_0)$ as a function of time⁹. $[Pi]_0$ and $[Pi]$ are the concentration of Pi at the zero time and the certain hydrolysis time, respectively.

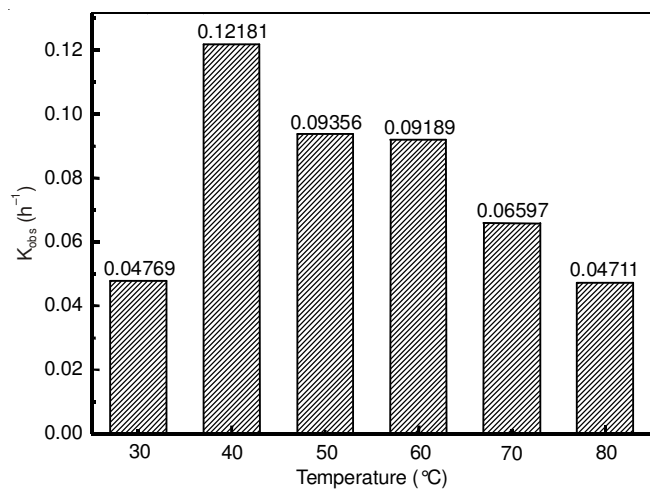


Fig. 6. Rate constants of ATP hydrolysis catalyzed by L in different temperature: pH = 4, $L_1 = ATP = 2 \times 10^{-4}$ mol/L

$$\ln([Pi]/[Pi]_0) = K_{obs}t$$

The rate constant (K_{obs}) of ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine is 4.77×10^{-2} , 12.18×10^{-2} , 9.36×10^{-2} , 9.19×10^{-2} , 6.60×10^{-2} and $4.71 \times 10^{-2} h^{-1}$ at the different temperature, respectively. At the beginning, the hydrolysis rate of ATP is accelerated with the rise of temperature. When the temperature is higher than 40 °C, the hydrolysis rate constant of ATP has a decrease by the increase of temperature. It's due to the interaction exists between 1,8-naphthalene diformate-L-histidine and ATP in aqueous solution²⁰. 1,8-Naphthalene diformate-L-histidine has a cationic side chain, which can interact with the phosphate oxygen atoms or the N-7 site of the adenine ring of ATP by hydrogen bonds and electrostatic interactions²¹. Weak non-covalent interaction between 1,8-naphthalene diformate-L-histidine and ATP exists. It is obvious that catalytic activity of 1,8-naphthalene diformate-L-histidine on ATP hydrolysis is better at 40 °C than at others. So, the following experiments were carried out at 40 °C.

pH value effect on ATP hydrolysis: The following tests were employed to study the hydrolysis of ATP catalyzed by 1,8-naphthalene diformate-L-histidine at low concentration for kinetic analysis. The reaction solutions were conducted at pH 2, 3, 4, 5, 6, 7, 8 and 9, respectively. The concentrations of both 1,8-naphthalene diformate-L-histidine and ATP were $2 \times 10^{-4} mol L^{-1}$. As illustrated in Figs. 7 and 8, the concentration of the products increases with time because ATP hydrolyzes in aqueous solution and its speed is largely accelerated by 1,8-naphthalene diformate-L-histidine.

The rate constant (K_{obs}) of ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine is 9.90×10^{-2} , 12.178×10^{-2} , 12.18×10^{-2} , 11.76×10^{-2} , 10.53×10^{-2} , 8.89×10^{-2} and $6.47 \times 10^{-2} h^{-1}$ at the different pH value, respectively. Moreover, these two figures can also show that hydrolysis rate of ATP in acid solution is larger than that in basic solution. When the pH value is higher than 6, the hydrolysis rate constant of ATP decreased quickly.

The results perhaps due to the interaction between the imidazole ring of histidine and γ -phosphorus or N-1 site of adenine ring of ATP²⁰. The N-1 site is a positive reaction center because N-1 is protonated when pH < 4. The carboxyl group of histidine is a negative center of the reaction because it has a

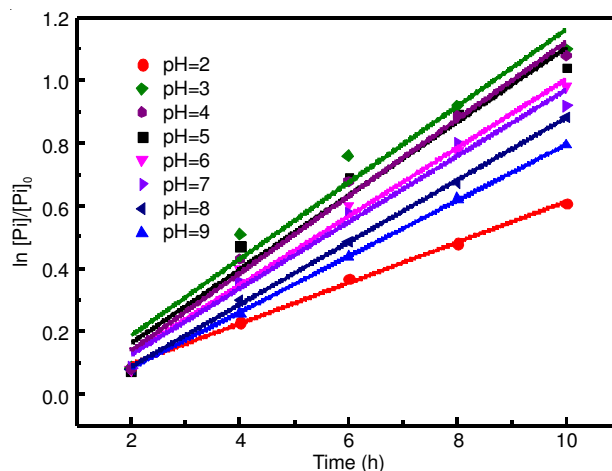


Fig. 7. Plot of $\ln([Pi]/[Pi]_0)$ as a function of time in different pH: T = 40 °C, $L_1 = ATP = 2 \times 10^{-4}$ mol/L

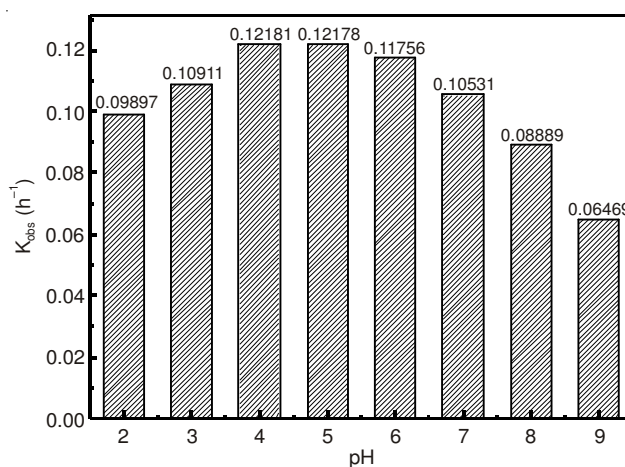


Fig. 8. Rate constants of ATP hydrolysis catalyzed by L in different pH: T = 40 °C, $L_1 = ATP = 2 \times 10^{-4}$ mol/L

negative charge in the whole pH range²³. Therefore, the carboxyl of histidine interacts with the N-1 site of ATP by hydrogen bond and electrostatic interactions. With increasing pH, N-1 is deprotonated, an inverse interaction takes place with and the protonated amine of 1,8-naphthalene diformate-L-histidine taking part in the interaction as a positive center²⁴. Intermolecular interactions between the carboxyl of 1,8-naphthalene diformate-L-histidine and ATP are impossible because there are no positive centers in the ATP molecule at relatively high pH²⁵. The phosphate group of ATP also engaged in noncovalent interactions with 1,8-naphthalene diformate-L-histidine, therefore, the hydrolysis rate of ATP is reduced slowly²⁶. Upon that, from the two figures, it's obvious that pH 4 was found to be optimum pH value for the process of catalytic hydrolysis of ATP. So, the following experiments were carried out at pH value 4.

According to the above experimental data, hydrogen bonding and electrostatic interaction is the key active force. As one of the half essential amino acids, the dissociation constant of imidazole group on histidine is 6. In other words, the proton concentration which was dissociated by histidine is more closer to water than that with other amino acids. In addition to this, the speed of provide and accept protons for imidazole are both fast.

Catalysis of 1,8-naphthalene diformate-L-histidine on ATP hydrolysis: As shown in Table-1, $10^2 K'_{\text{obs}}/\text{h}^{-1}$ and $10^2 K_{\text{obs}}/\text{h}^{-1}$ are the hydrolysis rate constant of ATP before and after the addition of 1,8-naphthalene diformate-L-histidine in different temperature, respectively. It is quite clear that hydrolysis rate constants of ATP achieve the maximum 0.1218 h^{-1} under the condition of the pH value is 4 and the temperature is 40°C after the addition of 1,8-naphthalene diformate-L-histidine. However, the hydrolysis rate constant of ATP is only $1.1041 \times 10^{-2} \text{ h}^{-1}$ without 1,8-naphthalene diformate-L-histidine in the same condition. Through calculation, the catalytic effect of 1,8-naphthalene diformate-L-histidine on ATP hydrolysis increased by about 11 times.

Table-2 shows the hydrolysis rate constant of ATP with and without 1,8-naphthalene diformate-L-histidine in different pH values. After the addition of 1,8-naphthalene diformate-L-histidine under the condition of pH value is 4 and the temperature is 40°C , the hydrolysis rate constant of ATP can be achieved to 0.1218 h^{-1} whereas the hydrolysis rate constant of ATP is only $1.0413 \times 10^{-2} \text{ h}^{-1}$ without 1,8-naphthalene diformate-L-histidine in the same condition. Conclusion should be obtained that it's 1,8-naphthalene diformate-L-histidine caused the 11.7 times rise of hydrolysis rate constant of ATP.

To sum up, though the hydrolysis of ATP in pure water solution is rather low, its speed is largely accelerated by 1,8-naphthalene diformate-L-histidine.

Tentative mechanism for ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine: Fig. 9 allows to considering tentative mechanisms for the molecular catalysis hydrolysis in L-ATP binary system. Catalytic efficiency depends on defined structural requirements of the complex itself, involving protonation pattern, electrostatic and hydrogen bonding effects, spatial arrangement of catalytic sites²⁷. The hydrolysis of ATP has been divided into four steps. In this system, the first step is the protonation of 1,8-naphthalene diformate-L-histidine and ATP. The N-7 site of the adenine ring of ATP and the nitrogen atom of the imidazole ring are both protonated²². The second step is recognition and binding among ATP and

1,8-naphthalene diformate-L-histidine. The third step involves the following intramolecular attack by acetate group on the protonated N-7 site of the adenine ring of ATP or intermolecular nucleophilic attack by the protonated nitrogen atom of the imidazole ring on Pg to form the intermediate and release of ADP²⁸. When 1,8-naphthalene diformate-L-histidine catalyzed ATP hydrolysis, the positive charge formed by asymmetric cleavage of terminal Pg transfers to the hydrogen atom of the imidazole ring, formed by phosphorylation of nucleophilic N atom, may be assigned as the phosphoramidate intermediate (PN)²⁹. The water molecule takes part in the catalytic process in different step with different functions. A proton releases to form a covalent N- PO_3^{2-} bond in the intermediate, which can be destroyed by the attack of a water molecule in the next step and the hydroxyl unit of water connects with PO_3^{2-} to give HPO_4^{2-} while the hydrogen atom comes back to the nucleophile (N atom) to form the protonated 1,8-naphthalene diformate-L-histidine again^{8,30}. Though the binding scheme in the complex is known, molecular models indicate that the size and shape of 1,8-naphthalene diformate-L-histidine and of ATP are compatible with such an arrangement.

Detail structural data are required to distinguish between these various possibilities and to establish the nature of the complexes formed. Work in progress should help to elucidate the pathways of ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine. It may involve a combination of the mechanisms and of the different complex species such as other amino acids. Histidine, as a key amino acid residue, locates in the active center of ATPase which catalyzes ATP synthesis/hydrolysis. The work herein will offer some useful information to explore the novel catalyst series for ATP hydrolysis.

Conclusion

A new functional catalyst, 1,8-naphthalene diformate-L-histidine, for ATP hydrolysis has been synthesized and characterized. At pH value 3, the quenching fluorescent intensity of 1,8-naphthalene diformate-L-histidine is the most obvious.

TABLE-1
COMPARISON OF HYDROLYSIS RATE CONSTANT OF ATP BEFORE AND AFTER THE ADDITION OF 1,8-NAPHTHALENE DIFORMATE-L-HISTIDINE IN DIFFERENT TEMPERATURE

pH	T ($^\circ\text{C}$)	$10^2 K'_{\text{obs}} (\text{h}^{-1})$	$10^2 K_{\text{obs}} (\text{h}^{-1})$	Multiple
4	30	0.8882	4.7691	5.3693
-	40	1.1041	12.1811	11.0335
-	50	2.3213	9.3562	4.0305
-	60	1.3735	9.1893	6.6902
-	70	1.5782	6.5972	4.1806
-	80	0.6208	4.7114	7.5886

TABLE-2
COMPARISON OF HYDROLYSIS RATE CONSTANT OF ATP BEFORE AND AFTER THE ADDITION OF 1,8-NAPHTHALENE DIFORMATE-L-HISTIDINE IN DIFFERENT pH VALUE

T ($^\circ\text{C}$)	pH	$10^2 K'_{\text{obs}} (\text{h}^{-1})$	$10^2 K_{\text{obs}} (\text{h}^{-1})$	Multiple
40	2	0.9830	9.8970	10.0682
-	3	1.0211	10.9112	10.6866
-	4	1.0413	12.1811	11.7013
-	5	1.1992	12.1782	10.157
-	6	2.2261	11.7561	5.2812
-	7	2.5502	10.5313	4.1298
-	8	1.6732	8.8890	5.3132
-	9	0.7162	6.4691	9.0349

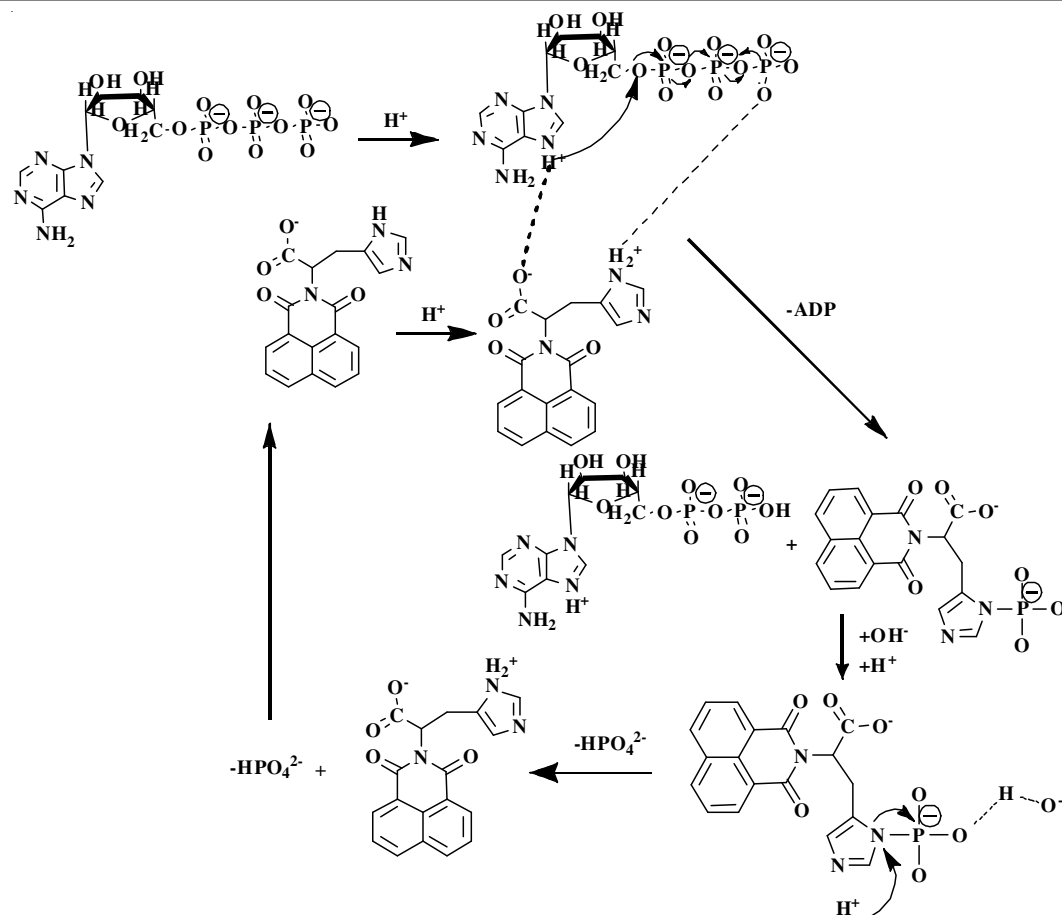


Fig. 9. Tentative mechanism for ATP hydrolysis catalyzed by 1,8-naphthalene diformate-L-histidine (L)

Meanwhile, we obtained the association constant $K_a = 6.72 \times 10^5 \text{ L mol}^{-1}$. 1,8-naphthalene diformate-L-histidine shows obvious catalytic activity on ATP hydrolysis at the aqueous. The hydrolysis rate constant is increased about 11.7 fold with addition of 1,8-naphthalene diformate-L-histidine and the best catalytic condition is at 40 °C and pH 4. The efficiency and selectivity of catalytic reactions and possible mechanism of ATP hydrolysis has been proposed.

ACKNOWLEDGEMENTS

The authors thank for the support by the High-Level Start-Up Funding of Shihezi University (RCZX200933, 2011BC008).

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