Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 795–805

STUDY ON COORDINATION BEHAVIOUR OF MANGANESE CHLORIDE WITH *L*-α-HISTIDINE

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(Received May 6, 2003; in revised form December 2, 2003)

Abstract

The reaction thermodynamic and kinetic equations for the non-reversible reactions are established. The enthalpy change of formation reaction of manganese(II) histidine (His) complex in water has been determined by microcalorimetry, using manganese chloride with *L*-α-histidine at 298.15–323.15 K. The standard enthalpy of formation of $Mn(His)_2^{2+}(aq)$ has been calculated. On the basis of experimental and calculated results, three thermodynamics parameters (the activation enthalpy, the activation entropy and the activation free energy), the rate constants, along with three kinetic parameters (the apparent activation energies, the pre-exponential constant and the reaction order) are obtained. The results show that the reaction easily takes place over the studied temperature range. The solid complex $Mn(His)_2Cl_2{\cdot}4H_2O$ was prepared and characterized by IR and TG-DTG.

Keywords: complex, formation reaction, L-α-histidine, manganese chloride, thermokinetics

Introduction

Manganese is an essential trace element for the living organisms. It is involved in a variety of matalloenzymes and participates in activating hundreds of other enzymes. Enzymes activated by manganese ion are closely associated with elimination of radicals, anti-aged, synthesis of amylose as well as procreation and growth. *L*-α-Amino acids are structural units of proteins. A better understanding of the complex of manganese and *L*-α-amino acids is thus of considerable practical and fundamental importance. It is expected that a desired additive of manganese would generated from the complexes of Mn(II) and amino acids. The complexes of manganese(II) and *L*-α-amino acids have been widely investigated in the literatures. Simeonova have investigated the stability constants and thermodynamic properties for the complexes of manganese with fifteen amino acids [1–3]. Quay and Basosi studied the properties of the complexes of manganese with amino acids in H_2O and D_2O by NMR and ESR [4, 5]. The catalytic activities of the complexes in H_2O_2 were discussed by Batry [6, 7], and the structure of the

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

complex of alanine and bromide was illustrated by Giunik [8]. Recently, thermochemistry behavior of solid complexes of $Mn(His)_2Cl_2\cdot 4H_2O$ was investigated in our research group [9]. In addition, kinetics of thermal decomposition of manganese(II) oxalate was reported [10]. However, the thermochemical properties and the formation thermokinetics of the complex of manganese and *L*-α-histidine have not been expounded in literature.

In this manuscript, the enthalpy change of formation reaction of manganese(II) histidine (His) complex in water has been determined by a microcalorimeter, using manganese chloride with *L*-α-histidine at 298.15–323.15 K, fundamental parameters for reaction of preparing manganese histidine complex, including the reaction rate constant (k), the activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_{\neq}^{\theta}$), the activation entropy ($\Delta S_{\neq}^{\theta}$), the activation free energie ($\Delta G_{\neq}^{\theta}$) and the enthalpy ($\Delta_r H_{\neq}^{\theta}$) were attained. The solid complex $Mn(His)_2Cl_2\cdot 4H_2O$ was prepared and characterized by IR and TG-DTG.

Experimental

Derivation of thermokinetics equations for the non-reversible reaction

In order to build up thermokinetics equations for the non-reversible reaction, a general mode of the reaction is depicted in following,

$$
\begin{array}{llll}
\multicolumn{4}{c}{A(aq)+B(aq)\ \text{or}\ B(s) \leftrightarrow [AB]^{\neq} \rightarrow \text{product+heat}} \\
t=0, & c_0=1 & c^{\neq} & \alpha=0 \quad H_0=0 \\
t=t, & c_i & & \alpha_i \quad H_i \\
t=\infty, & c_\infty & & \alpha=1 \quad H_\infty
\end{array}
$$

The relationship of reaction system energy with reaction process is attained from boundary conditions,

$$\frac{c_0-c_i}{c_0-c_\infty}=\frac{0-\alpha_i}{0-\alpha_\infty}=\frac{0-H_i}{0-H_\infty} \tag{1}$$

and

$$\alpha=\frac{H_i}{H_\infty} \tag{2}$$

$$\frac{d\alpha}{dt}=\frac{1}{H_\infty}\frac{dH_i}{dt} \tag{3}$$

Equation (4) is deduced from introducing Eqs (2) and (3) to the differential equation for n^{th} order reaction

$$\frac{1}{H_\infty}\frac{\mathrm{d}H_\mathrm{i}}{\mathrm{d}t}=k(1-\alpha)^\mathrm{n} \tag{4}$$

furthermore,

$$\frac{1}{H_\infty}\frac{\mathrm{d}H_\mathrm{i}}{\mathrm{d}t}=k\left(1-\frac{H_\mathrm{i}}{H_\infty}\right)^\mathrm{n} \tag{5}$$

$$\ln\left(\frac{1}{H_\infty}\frac{\mathrm{d}H_\mathrm{i}}{\mathrm{d}t}\right)=\ln k+n\ln\left(1-\frac{H_\mathrm{i}}{H_\infty}\right) \tag{6}$$

So, the reaction rate constant k and the reaction order n are procured from thermokinetics experimental data by linear least square fitting.

$$\ln k=\ln A-\left(\frac{E}{RT}\right) \tag{7}$$

According to Arrhenius Eq. (7) and the value k with temperature changing, the apparent activation energy E and the pre-exponential constant A are calculated out.

From the absolute rate theory, quantum theory and energy distribution theory, the Eq. (8) is given,

$$-\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t}=\frac{c^{\neq}}{\tau}v=v[\mathrm{AB}]^{\neq}=\frac{\varepsilon}{h}[\mathrm{AB}]^{\neq}=\frac{k_\mathrm{B}T}{h}[\mathrm{AB}]^{\neq}=\frac{kT}{N_\mathrm{A}h}[\mathrm{AB}]^{\neq} \tag{8}$$

where v is the vibration frequency. It is assumed that a molecular of $c^{\neq}$ is dissociated after one vibration. ε is the vibration freedom energy, h Planck constant, k_B Boltzmann constant and N_A Avogadro constant.

As we know, the relationship between the reaction rate and concentration is represented,

$$-\frac{\mathrm{d}[\mathrm{AB}]}{\mathrm{d}t}=k[\mathrm{A}][\mathrm{B}] \tag{9}$$

When the reaction comes to the equilibrium, we have

$$[\mathrm{AB}]^{\neq}=K^{\neq} \tag{10}$$

The combination of the Eqs (8)–(10) gives

$$k=\frac{RT}{N_\mathrm{A}h}K^{\neq} \tag{11}$$

To the reaction system the basic thermodynamic Eqs (12) and (13) exist.

$$\Delta G_{\neq}=-RT\ln K^{\neq} \tag{12}$$

$$\Delta G_{\neq}^{\theta}=\Delta H_{\neq}^{\theta}-T\Delta S_{\neq}^{\theta} \tag{13}$$

Connecting the Eqs (11) and (12), Eq. (14) is derived.

$$\Delta G_{\neq}^{\theta}=RT\ln\left(\frac{RT}{Nhk}\right) \tag{14}$$

while Eq. (15) is from the combination of the Eqs (11)–(13).

$$k=\frac{RT}{N_{\mathrm{A}}h}\mathrm{e}^{-\Delta G_{\neq}^{\theta}/RT}=\frac{RT}{N_{\mathrm{A}}h}\mathrm{e}^{(T\Delta S_{\neq}^{\theta}-\Delta H_{\neq}^{\theta})/RT}=\frac{RT}{N_{\mathrm{A}}h}\mathrm{e}^{\Delta S_{\neq}^{\theta}/R}\,\mathrm{e}^{-\Delta H_{\neq}^{\theta}/RT} \tag{15}$$

Finally, Eq. (16) is set up.

$$\ln\left(\frac{k}{T}\right)=\ln\left(\frac{k_{\mathrm{B}}}{h}\right)+\frac{\Delta S_{\neq}^{\theta}}{R}-\frac{\Delta H_{\neq}^{\theta}}{RT} \tag{16}$$

$\Delta H_{\neq}^{\theta}$ and $\Delta S_{\neq}^{\theta}$ are thus available by linear least square regression.

In conclusion, the reaction thermodynamic and kinetic parameters for the non-reversible reactions are procured from the Eqs (6), (7), (14) and (16) at constant pressure and isothermal conditions.

Materials

The $MnCl_2\cdot6H_2O$ (A) is of A.R. grade. *L*-α-histidine (B) is of B.R. grade with the >99.5% purity. They are dissolved in distilled water. The molarities of solution A and B are 0.1000 mol L^{-1}. In our experiments, the molar ratio of two solutions, A to B is l:2. The conductivity of the deionized water is $5.48\cdot10^{-8}$ S cm^{-1}.

Experimental equipment and conditions

The reaction thermokinetics was executed by a microcalorimeter, type RD496-III (China, Southwest Institute of Electronic Engineering), which was equipped with two 15 mL vessels (Fig. 1) [9]. After reaching equilibrium, the spacers of the sample and reference vessels were pushed down simultaneously and the samples were mixed. The microcalorimeter was calibrated by Joule effect and its sensitivity were (63.994±0.042), (64.308±0.027), (64.499±0.064), (64.638±0.078), (64.733±0.077) and (64.739±0.059) μV mW^{-1} at the experimental temperatures of (298.15±0.005), (303.15±0.005), (308.15±0.005), (313.15±0.005), (318.15±0.005) and (323.15 ±0.005) K, respectively. The experimental precision and accuracy were checked by measuring the enthalpy of special purity crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta}$ of (17.238±0.048) kJ mol^{-1} (*t* test, 99% confidence) is the best agreement with that of (17.241±0.018) kJ mol^{-1} reported in [10]. This indicated that the device used in this work was reliable. The precision measured was in 0.5%.

The IR spectra for the complex of manganese and histidine were determined by the Bruker of USA, Model EQ Uinox-550 FT-IR spetrophotometer (KBr pellet). The content of Mn^{2+} was determined by ammonium peroxydisulfate oxidation method. The content of Cl^{-} was determined by Fajans method. Carbon, hydrogen, and nitrogen

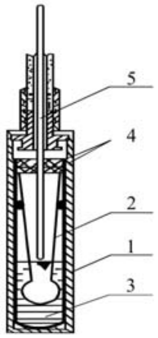

Fig. 1 Device used for the study of the formation reaction; 1 – calorimetric cell; 2 – adding tube containing manganese chloride solution; 3 – adding tube containing histidine solution; 4 – silicone rubber cover; 5 – glass rod (on depressing the bottom of tube 2 is broken. The two solutions are mixed in the 1

analyses were carried out on a 2400-type elemental analyzer of Perkin Elmer Company. TG-DTG data were obtained simultaneously by using a Perkin Elmer thermogravimetric analyzer. The TG-DTG runs were carried out under a dynamic atmosphere of dry oxygen at flow rate of 60 mL min^{-1}. The heating rate used was 10°C min^{-1}. Sample mass was about 1 mg.

Results and discussion

Determination of $\Delta_r H_m^\theta$ *and calculation of* $\Delta_{f,Cu(His)_2^{2+}(aq)} H_m^\theta$

The following Eq. (a) could represent the formation reaction of manganese histidine complex:

$$\mathrm{Mn}^{2+}(aq)+2\mathrm{His}(aq)\rightarrow\mathrm{Mn(His)}_2^{2+}(aq) \qquad \text{(a)}$$

Within the range of the experimental temperature, the reaction is an endothermic one. $\Delta_r H_m^\theta$ of the reaction was measured six times, at 298.15 K. It was 0.122, 0.121, 0.121, 0.121, 0.121 and 0.120 kJ mol^{-1}, respectively, mean value was (0.121 0.001) kJ mol^{-1}. According to Hess' law, the standard enthalpy of formation of $\mathrm{Mn(His)}_2^{2+}(aq)$ was calculated through Eq. (a):

$$\begin{aligned}\Delta_{f,Mn(His)_2^{2+}(aq)} H_m^\theta &= \Delta_r H_m^\theta + (\Delta_{f,Mn^{2+}(aq)} H_m^\theta + 2\Delta_{f,L\text{-}\alpha\text{-}His(aq)} H_m^\theta) \\ &= [(0.121\pm0.001)+(-220.75)+2\times(-424.91\pm1.54)]\ \mathrm{kJ\ mol^{-1}} \\ &= (-1070.45\pm3.08)\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Here, $\Delta_{f,Mn^{2+}(aq)} H_m^\theta$ is from [11] and $\Delta_{f,L\text{-}\alpha\text{-}His(aq)} H_m^\theta$ from [12].

Table 1 Thermographic data of the reaction for manganese chloride and *L*-α-histidine

t/s	298.15 K		303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	H_i/H_0 10^4/J s^{-1}	dH_i/dt	H_i/H_0 10^4/J s^{-1}	dH_i/dt	H_i/H_0 10^4/J s^{-1}	dH_i/dt	H_i/H_0 10^4/J s^{-1}	dH_i/dt	H_i/H_0 10^4/J s^{-1}	dH_i/dt	H_i/H_0 10^4/J s^{-1}	dH_i/dt
200	0.3184	4.232	0.2304	8.185	0.2655	11.48	0.2256	14.34	0.2290	19.19	0.1674	23.10
250	0.4073	4.017	0.3105	7.893	0.2997	10.96	0.2997	13.89	0.3013	18.47	0.2501	22.41
300	0.4871	3.747	0.3859	7.507	0.3695	10.34	0.3695	13.27	0.3696	17.57	0.3148	21.02
350	0.5578	3.488	0.4555	7.051	0.4344	9.705	0.4344	12.58	0.4335	16.59	0.3778	19.64
400	0.6200	3.224	0.5194	6.601	0.4945	9.075	0.4945	11.83	0.4928	15.73	0.4556	18.50
450	0.6744	2.981	0.5776	6.179	0.5497	8.489	0.5497	11.13	0.4524	14.75	0.5129	17.65
500	0.7220	2.739	0.6306	5.769	0.6001	7.919	0.6001	10.48	0.5981	13.89	0.5685	16.78
550	0.7633	2.522	0.6785	5.361	0.6461	7.380	0.6461	9.856	0.6445	13.07	0.6129	15.66
600	0.7993	2.320	0.7217	4.974	0.6880	6.886	0.6880	9.179	0.6868	12.26	0.6690	14.54
650	0.8304	2.129	0.7606	4.643	0.7259	6.423	0.7259	8.622	0.7253	11.52	0.7193	13.33

H_0=0.142 (298.15 K), 0.226 (303.15 K), 0.252 (308.15 K), 0.306 (313.15 K), 0.356 (318.15 K) and 0.362 J (323.15 K)

Table 2 The values of n, k, A, E, $\Delta G^{\theta}_{\neq}$, $\Delta H^{\theta}_{\neq}$ and $\Delta S^{\theta}_{\neq}$ of the reaction for manganese chloride and *L*- -histidine

T/K	Eq. (6)			Eq. (7)			Eq. (14)	Eq. (16)		
	$k\cdot10^3$/s^{-1}	n	r^*	E/kJ mol^{-1}	ln$A$	r^*	$\Delta G^{\theta}_{\neq}$/kJ mol^{-1}	$\Delta H^{\theta}_{\neq}$/kJ mol^{-1}	$\Delta S^{\theta}_{\neq}$/kJ mol^{-1}	$r^{\neq}$
298.15	3.680	0.502	0.999	20.68	2.733	0.999	86.92	17.95	–265.0	0.997
303.15	4.201	0.500	0.998				88.08			
308.15	4.798	0.504	0.998				89.24			
313.15	5.416	0.503	0.999				90.41			
318.15	6.189	0.505	0.997				91.55			
323.15	7.026	0.509	0.998				92.69			

*r – the correlation coefficient

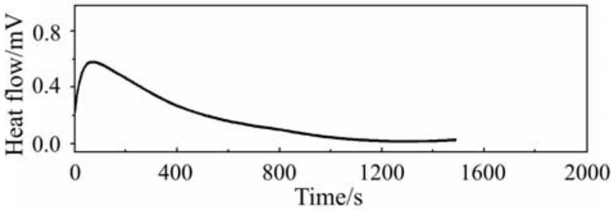

Fig. 2 Thermokinetic curve of the reaction for manganese chloride and *L*-α-histidine (298.15 K)

The thermokinetics calculation of the formation reaction

The typical thermokinetic (*TK*) curve of the reaction was shown in Fig. 2. The original data obtained from the *TK* curve were presented in Table 1.

According to the Eqs of (6), (7), (14) and (16), the reaction rate constant (*k*), the activation energy (*E*), the pre-exponential constant (*A*), the reaction order (*n*), the activation enthalpy ($\Delta H_{\neq}^{\theta}$), the activation entropy ($\Delta S_{\neq}^{\theta}$), the activation free energy ($\Delta G_{\neq}^{\theta}$) and the enthalpy ($\Delta_r H_{\neq}^{\theta}$) are attained, which were presented in Table 2.

The results in Table 2 indicate that the rate of the reaction increases with the temperature increasing, the reaction is of the first order, and the values of E and $\Delta H_{\neq}^{\theta}$ are very low and $\Delta S_{\neq}^{\theta}$ is high. These observations show that the title reaction easily proceeds over the temperature range of 298.15–323.15 K, as is the reaction of $CrCl_3$ with histidine [13], which is consistent with the large hydroenthalpy and small formation enthalpy of $Mn(His)_2^{2+}$.

Preparation and composition of the complex

The final solution collected from each experiment was concentrated at a 343~353 K water bath till crystal membrane formed on the surface, then it was put into a containing P_2O_5 desiccator drying to constant mass.

The analytical results inflect that they have the identical composition of $Mn(His)_2Cl_2 \cdot 4H_2O$. The analytical results of composition are summarized in Table 3.

Table 3 Analytical results of composition of solid complex (/%)

	Mn^{2+}	Cl^-	C	H	N
Calculated values	10.81	13.96	28.36	5.16	16.54
Experimental values	10.79	14.02	28.39	5.21	16.51

The IR absorption of main groups for complex and ligand are given in Table 4.

The IR spectrum for the complex shows that characteristic absorption peaks of amino and carboxyl groups have a great shift as compared to those in the ligand. It indicates that nitrogen and oxygen atoms in the complex coordinate to Mn^{2+} in a bidentate fashion. In addition to above, characteristic absorption peak of imidazolyl group in the complex shifts intensively. This shows that nitrogen atom in the

Table 4 IR absorption of main groups for solid complex and ligand/cm^{-1}

Compound	$\nu^{as}_{NH_3^+}$ $\nu^{as}_{NH_2}$	$\nu^{s}_{NH_3^+}$ $\nu^{s}_{NH_2}$	$\delta^{as}_{NH_3^+}$ $\delta^{as}_{NH_2}$	$\delta^{s}_{NH_3^+}$ $\delta^{s}_{NH_2}$	$\nu^{as}_{COO^-}$	$\nu^{s}_{COO^-}$	OH	ν^{as}_{CCN}	ν^{s}_{CCN}
L-α-His	3025	2860	1590	1456	1635	1415	–	1315	744
$Mn(His)_2Cl_2{\cdot}4H_2O$	3116	3011	1629	1409	1499	1332	3420 811	1082	956

imidazolyl group coordinates to Mn^{2+} as well. 3420 and 811 cm^{-1} in the IR spectrum for the complex are assigned to hydroxyl absorption of water. The existence of water molecule in the complex is believed.

Thermostability of the solid complex

The TG-DTG curve of the solid complex of $Mn(His)_2Cl_2{\cdot}4H_2O$ are presented in Fig. 3. The data on the decomposition products, decomposition temperatures and residue obtained from the Fig. 3 are listed in Table 5.

Table 5 Data on thermal decomposition of the complex

Product	Decomposition temperature/°C	Residue/%
$Mn(His)_2Cl_2{\cdot}1.5H_2O$	51–360	91.52 (91.54)[a]
$Mn(His)_2Cl_2{\cdot}MnCl_2$	360–650	55.37 (55.29)
$MnCl_2$	650–840	24.49 (22.76)

[a] The data in brackets are calculated values

Table 5 and Fig. 3 allow the following confirmations:

(1) The mass loss values in the processes of the thermal decomposition are close to the calculated values.

(2) The thermal decomposition processes proceeds in three steps. The first step is the loss of the part of crystal water from the complex. The following step is that part of the complex is discomposed into $MnCl_2$, the mixture of $MnCl_2$ and $Mn(His)_2Cl_2$ is obtained. At the last step, the complex is discomposed into $MnCl_2$ completely.

In order to attest the decomposition processes mentioned above, the intermediates and final products of the thermal decomposition of the complex was identified

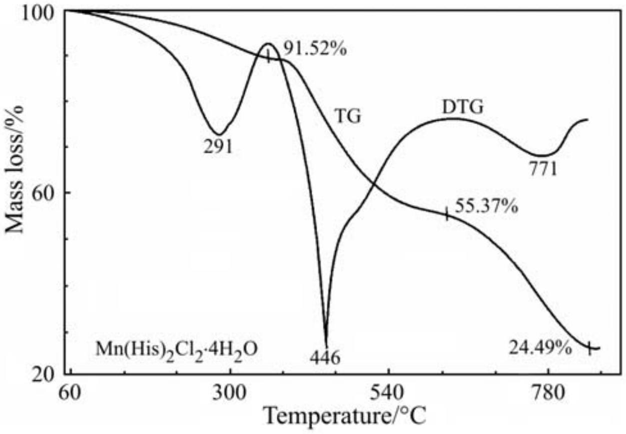

Fig. 3 TG-DTG curve of the solid complex of $Mn(His)_2Cl_2{\cdot}4H_2O$

via IR spectrophotometry. IR spectra of these compound are in good agreement with the characteristic peaks of $Mn(His)_2Cl_2$, $Mn(His)_2Cl_2$ and $MnCl_2$, $MnCl_2$. Therefore, it is reasonable to get the above results for the decomposition processes of the complex.

Conclusions

- Based on the basic thermodynamic equations, a set of thermokinetics models is developing for non-reversible reactions at constant temperature and pressure.
- On the basis of experimental and calculated results, the reaction order of the formation of $Mn(His)_2Cl_2 \cdot 4H_2O$ over the studied temperature range is found to be of the first one and the reaction is exothermic. The enthalpy change of the reaction is (0.121±0.001) kJ mol^{-1}, the standard enthalpy of formation of $Mn(His)_2^{2+}(aq)$ is (–1070.45±3.08) kJ mol^{-1}.
- The activation energy of the formation reaction of $Mn(His)_2Cl_2 \cdot 4H_2O$ over the range of 298.15–323.15 K is very small, and the entropy of the formation reaction of $Mn(His)_2Cl_2 \cdot 4H_2O$ is high. The title reaction easily takes place at 298.15–323.15 K, which contributes to strong coordination force of histidine.

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We thank National Science Foundation of China and National Science Foundation of Shaanxi Province for financial support.

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