[Article]

doi: 10.3866/PKU.WHXB201307153

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3-硝基-1,3,4-三唑-5-酮金属(Li, Na, Pb, Cu)盐的 制备反应热动力学

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摘要: 在常压、298.15 K条件下, 用RD496-2000微量热仪开展了3-硝基-1,3,4-三唑-5-酮(NTO)金属(Li, Na, Pb, Cu)盐制备反应的热动力学研究, 得到了反应过程中的热力学参数(活化焓、活化熵和活化自由能), 速率常数和动力学参数(活化能、指前因子和反应级数), 还得到了在25–40 °C范围内NTO金属(Li, Na, Pb, Cu)盐制备反应过程的反应焓. 结果表明, NTO金属(Li, Na, Pb, Cu)盐的制备反应较容易发生. 基于Hess定律, 得到了 $\Delta_f H_m^\circ(\text{Li(NTO)} \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ 和 $\Delta_f H_m^\circ(\text{Na(NTO)} \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ 的值.

关键词: NTO金属盐; 制备反应; 微量热仪; 热动力学

中图分类号: O643; O642

Thermokinetics of the Formation Reactions of Metal (Li, Na, Pb, Cu) Salts of 3-Nitro-1,2,4-triazol-5-one

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Abstract: The thermokinetics of the formation reactions of metal (Li, Na, Pb, Cu) salts of 3-nitro-1,2,4-triazol-5-one (NTO) was studied using a microcalorimeter. On the basis of experimental and calculated results, three thermodynamic parameters (activation energy, pre-exponential constant, and reaction order), rate constant, three thermokinetic parameters (activation enthalpy, activation entropy, and activation free energy) and the enthalpies of the reactions to prepare the metal salts of NTO in the temperature range of 25–40 °C were obtained. The title reactions occur easily in the studied temperature range. Based on Hess' law, the values of $\Delta_f H_m^\circ(\text{Li(NTO)} \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f H_m^\circ(\text{Na(NTO)} \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ are obtained.

Key Words: Metal salts of 3-nitro-1,2,4-triazol-5-one; Formation reaction; Microcalorimeter; Thermokinetics

1 Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) as a high-energy and low-sensitivity explosive is currently receiving increasing attention.^{1–4} Its metal salts are also energetic materials and have been used as energetic combustion catalysts in propellants.⁵ The synthe-

sis, chemical structure, and properties of various salts have been reported.^{6–15} However, the formation thermokinetics of salts of NTO have not been reported.

In this work, the fundamental parameters for the four reactions of preparing metal (Li, Na, Pb, Cu) salts of NTO, includ-

Received: June 3, 2013; Revised: July 15, 2013; Published on Web: July 15, 2013.

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The project was supported by the National Natural Science Foundation of China (21173163) and Technology Foundation of Laboratory of Propellant and Explosive Combustion in China (9140C350307110C3506).

国家自然科学基金(21173163)和燃烧与爆炸技术重点实验室基金(9140C350307110C3506)资助项目

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ing the reaction rate constant (k), the activation energy (E), the pre-exponential constant (A), the reaction order (n), the activation enthalpy ($\Delta H_{\neq}$), the activation entropy ($\Delta S_{\neq}$), the activation free energy ($\Delta G_{\neq}$), and the enthalpies (ΔH_f) were obtained by means of a RD496-2000 Calvet microcalorimeter. These parameters will provide a scientific basis for technological processing of preparing metal (Li, Na, Pb, Cu) salts of NTO.

2 Experimental

2.1 Materials

NTO (A), $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$ (B), and $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$ (C) used in the experiment were prepared by Xi'an Modern Chemistry Research Institute, their purities were more than 99.5%. The water was twice distilled before use. LiOH (D), NaOH (E), sulfate copper (G), and lead nitrate (H) were all analytically pure. They were all dissolved in distilled water. The molarity of solution A was $0.13 \text{ mol} \cdot \text{L}^{-1}$. The molarities of solutions B and C were all $0.18 \text{ mol} \cdot \text{L}^{-1}$. The molarities of solutions D and E were all $0.15 \text{ mol} \cdot \text{L}^{-1}$. The molarities of solutions G and H were all $0.14 \text{ mol} \cdot \text{L}^{-1}$. In our experiment, the molar ratios of solution A to solution D, solution A to solution E, and solution A to solution F were all 1:1. The molar ratios of both solution G to solution B and solution H to solution C were 1:2.

2.2 Experimental equipment and conditions

The thermokinetics of the formation reactions of metal (Li, Na, Pb, Cu) salts of NTO were measured by a Calvet microcalorimeter (Mianyang CAEP Thermal Analysis Instrument Company, China),¹⁶⁻¹⁹ which had a sensitivity of $66.5 \mu\text{V} \cdot \text{mW}^{-1}$ and was equipped with two 15 mL vessels. The microcalorimeter was calibrated by the Joule effect, and the calibration was re-

peated after each experiment. The precision of enthalpy measurement is 2%. The measurements of the formation reactions were all carried out at 25, 30, 35, and 40 °C. Each process was repeated four times to ensure the precision of the data.²⁰⁻²² Vari-oE III element analysis equipment from German was employed to detect the contents of C, N, O, and H. Metal contents were measured with a S4 Pioneer X-ray fluorescence spectrometer.

3 Results and discussion

3.1 Element analysis

The elemental analysis results on $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$, $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ are listed in Table 1. They are in good agreement with the formulae proposed for these salts.

3.2 Thermokinetic parameters of the formation reactions of metal (Li, Na, Pb, Cu) salts of NTO

The original data are shown in Table 2. These experimental data were put into the thermokinetic equation (1) obtained by

Table 1 Elemental analysis results on metal salts of NTO

Salt		Content/%				
		C	H	O	N	metal
$\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$	calculated	13.96	2.93	46.51	32.57	4.03
	found	13.65	2.87	47.03	32.61	3.84
$\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$	calculated	14.13	1.78	37.62	32.59	13.52
	found	13.57	1.75	37.76	33.71	13.21
$\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$	calculated	9.94	0.83	23.18	23.18	42.87
	found	9.65	0.79	24.51	23.09	41.96
$\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$	calculated	13.43	1.68	35.80	31.33	17.76
	found	13.21	1.63	36.07	31.51	17.58

Table 2 Thermokinetic data of formation reaction for metal salts of NTO*

t/s	298.15 K			303.15 K			308.15 K			313.15 K		
	$-(\text{d}H/\text{d}t)_t$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(H/H_0)_t$	ΔH_m ($\text{kJ} \cdot \text{mol}^{-1}$)	$-(\text{d}H/\text{d}t)_t$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(H/H_0)_t$	ΔH_m ($\text{kJ} \cdot \text{mol}^{-1}$)	$-(\text{d}H/\text{d}t)_t$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(H/H_0)_t$	ΔH_m ($\text{kJ} \cdot \text{mol}^{-1}$)	$-(\text{d}H/\text{d}t)_t$ ($\text{mJ} \cdot \text{s}^{-1}$)	$(H/H_0)_t$	ΔH_m ($\text{kJ} \cdot \text{mol}^{-1}$)
$\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$												
200	0.7334	0.3742	-39.12	0.7803	0.4201	-38.59	0.9093	0.2177	-35.88	0.9141	0.2450	-37.27
300	0.6065	0.5139		0.6155	0.5567		0.7483	0.3768		0.7871	0.4179	
400	0.4911	0.6275		0.4703	0.6631		0.5979	0.5108		0.6569	0.5605	
500	0.4026	0.7172		0.3495	0.7441		0.4532	0.6178		0.4815	0.6719	
600	0.3106	0.7868		0.2596	0.8052		0.3506	0.7015		0.3627	0.7566	
700	0.2407	0.8401		0.1903	0.8509		0.2706	0.7664		0.2702	0.8200	
800	0.1818	0.8806		0.1498	0.8849		0.2084	0.8163		0.2001	0.8671	
900	0.1278	0.9111		0.1021	0.9102		0.1608	0.8548		0.1477	0.9020	
1000	0.0951	0.9341		0.0831	0.9293		0.1242	0.8845		0.1085	0.9276	
1100	0.0791	0.9513		0.0685	0.9435		0.0965	0.9076		0.0795	0.9464	
1200	0.0599	0.9642		0.0533	0.9542		0.0735	0.9255		0.0585	0.9602	
1300	0.0457	0.9738		0.0459	0.9625		0.0594	0.9396		0.0431	0.9704	
1400	0.0323	0.9811		0.0419	0.9690		0.0443	0.9507		0.0319	0.9779	
1500	0.0225	0.9865		0.0351	0.9742		0.0359	0.9596		0.0218	0.9835	
1600				0.0297	0.9785		0.0276	0.9667		0.0178	0.9877	
1700				0.0275	0.9822		0.0201	0.9725		0.0127	0.9908	

to be continued

continued Table 2

<i>t</i> /s	298.15 K			303.15 K			308.15 K			313.15 K		
	$-(dH/dt)_t$ (mJ·s ⁻¹)	(<i>H</i> / <i>H</i> ₀) _{<i>t</i>}	$\Delta_f H_m$ (kJ·mol ⁻¹)	$-(dH/dt)_t$ (mJ·s ⁻¹)	(<i>H</i> / <i>H</i> ₀) _{<i>t</i>}	$\Delta_f H_m$ (kJ·mol ⁻¹)	$-(dH/dt)_t$ (mJ·s ⁻¹)	(<i>H</i> / <i>H</i> ₀) _{<i>t</i>}	$\Delta_f H_m$ (kJ·mol ⁻¹)	$-(dH/dt)_t$ (mJ·s ⁻¹)	(<i>H</i> / <i>H</i> ₀) _{<i>t</i>}	$\Delta_f H_m$ (kJ·mol ⁻¹)
Na(NTO)·H ₂ O												
300	0.6686	0.4121	−37.79	0.7601	0.3631	−39.88	0.8067	0.3845	−36.98	0.9686	0.3737	−38.20
400	0.5351	0.5441		0.6563	0.4995		0.6547	0.5165		0.7955	0.5072	
500	0.4201	0.6492		0.5168	0.6092		0.4436	0.6217		0.6245	0.6133	
600	0.3253	0.7309		0.4093	0.6951		0.3452	0.7039		0.4457	0.6957	
700	0.2506	0.7935		0.3149	0.7615		0.2665	0.7675		0.3386	0.7589	
800	0.1804	0.8410		0.2408	0.8124		0.2052	0.8166		0.2583	0.8072	
900	0.1342	0.8771		0.1841	0.8514		0.1583	0.8544		0.1968	0.8440	
1000	0.1004	0.9044		0.1411	0.8812		0.1224	0.8836		0.1520	0.8723	
1100	0.0791	0.9252		0.1085	0.9040		0.0951	0.9062		0.1198	0.8941	
1200	0.0664	0.9409		0.0837	0.9216		0.0744	0.9238		0.0917	0.9111	
1300	0.0496	0.9530		0.0650	0.9352		0.0586	0.9376		0.0752	0.9245	
1400	0.0389	0.9623		0.0511	0.9459		0.0466	0.9486		0.0585	0.9352	
1500	0.0338	0.9695		0.0407	0.9543		0.0374	0.9573		0.0483	0.9440	
1600	0.0287	0.9752		0.0327	0.9610		0.0303	0.9643		0.0389	0.9513	
1700							0.0247	0.9701		0.0352	0.9576	
Pb(NTO) ₂ ·H ₂ O												
100	0.0268	0.1023	1.45			1.42			1.37			1.49
150	0.0258	0.2435										
200	0.0236	0.3857										
250	0.0207	0.5144		0.0263	0.4293		0.0287	0.4018		0.0276	0.3680	
300	0.0164	0.6249		0.0228	0.5250		0.0251	0.4918		0.0240	0.4476	
350	0.0144	0.7169		0.0197	0.6063		0.0215	0.5716		0.0203	0.5165	
400	0.0112	0.7920		0.0163	0.6736		0.0190	0.6410		0.0168	0.5756	
450	0.0088	0.8520		0.0138	0.7289		0.0166	0.7005		0.0147	0.6262	
500	0.0065	0.8994		0.0105	0.7741		0.0135	0.7511		0.0119	0.6695	
550	0.0050	0.9360		0.0086	0.8111		0.0117	0.7936		0.0099	0.7065	
600	0.0035	0.9638		0.0073	0.8418		0.0098	0.8294		0.0080	0.7384	
650	0.0029	0.9729		0.0064	0.8675		0.0079	0.8591		0.0072	0.7663	
700				0.0054	0.8893		0.0068	0.8840		0.0064	0.7921	
750				0.0044	0.9078		0.0057	0.9047		0.0053	0.8163	
800				0.0038	0.9238		0.0043	0.9219		0.0046	0.8383	
Cu(NTO) ₂ ·2H ₂ O												
300	0.1613	0.4026	−11.29	0.1781	0.3541	−11.39	0.1858	0.4035	−10.92	0.1864	0.3489	−10.71
400	0.1333	0.5371		0.1499	0.4844		0.1607	0.5480		0.1524	0.4808	
500	0.0970	0.6447		0.1108	0.5923		0.1293	0.6647		0.1103	0.5899	
600	0.0746	0.7285		0.0893	0.6787		0.0863	0.7555		0.0794	0.6773	
700	0.0567	0.7924		0.0685	0.7473		0.0698	0.8249		0.0526	0.7462	
800	0.0429	0.8409		0.0489	0.8011		0.0535	0.8772		0.0458	0.8002	
900	0.0324	0.8775		0.0381	0.8431		0.0354	0.9165		0.0328	0.8422	
1000	0.0245	0.9052		0.0294	0.8757		0.0260	0.9457		0.0240	0.8749	
1100	0.0186	0.9262		0.0225	0.9008		0.0155	0.9671		0.0196	0.9002	
1200	0.0142	0.9421		0.0174	0.9201		0.0089	0.9824		0.0157	0.9203	
1300	0.0119	0.9544		0.0147	0.9351		0.0048	0.9929		0.0124	0.9360	
1400	0.0089	0.9639		0.0116	0.9467					0.0097	0.9484	
1500	0.0067	0.9713		0.0089	0.9558					0.0077	0.9582	
1600	0.0052	0.9771		0.0071	0.9631					0.0065	0.9663	

* $\Delta_f H_m$ denotes the enthalpies of formation reactions for metal salts of NTO.

the equation of the reaction of the n th order and the relation between the energy change of a reacting system and the extent of reaction by linear least-squares method.^{23,24}

$$\ln \left[\frac{1}{H_t} \left(\frac{dH}{dt} \right) \right] = \ln k + n \ln \left[1 - \left(\frac{H_t}{H_0} \right) \right] \quad i=1, 2, \dots, L \quad (1)$$

where H_t is the total reaction heat; H_i is the reaction heat in a certain time; dH/dt is the exothermic rate at time t ; k is the rate constant of prepared reaction; n is the reaction order.

The values of k and n obtained by Eq.(1), the values of E and A obtained by Eq.(2), the value of ΔG° obtained by Eq.(3), and the values of ΔH° and ΔS° obtained by Eq.(4) are all listed in Table 3.

$$\ln k = \ln A - \frac{E}{RT} \quad (2)$$

$$\Delta G^\circ = RT \ln \frac{RT}{Nhk} \quad (3)$$

and

$$\ln \frac{k}{T} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln \frac{k_B}{h} \quad (4)$$

where R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T the absolute temperature; N the Avogadro number ($6.024 \times 10^{23} \text{ mol}^{-1}$); h Planck's constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}^{-1}$); k_B the Boltzmann's constant ($1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$).

The formation reactions of Li, Na, and Cu salts of NTO were exothermic ones, but the formation reaction of preparing Pb salt of NTO was an endothermic one. The results in Tables 2 and 3 clearly indicated that the higher the temperature of the four reactions, the faster the rate of reactions and the title reac-

tions were of the first order.

The values of E and A for the formation reaction were $15.29 \text{ kJ} \cdot \text{mol}^{-1}$ and 0.07 s^{-1} for $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$; $11.79 \text{ kJ} \cdot \text{mol}^{-1}$ and 0.02 s^{-1} for $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$; $4.21 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{-2.89} \text{ s}^{-1}$ for $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$; $7.59 \text{ kJ} \cdot \text{mol}^{-1}$ and $10^{-2.49} \text{ s}^{-1}$ for $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$.

The meanvalues of ΔH° , ΔS° , and ΔG° for the formation reactions of metal salts of NTO in the temperature range $25\text{--}40^\circ\text{C}$ are $12.75 \text{ kJ} \cdot \text{mol}^{-1}$, $-275.62 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $96.99 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$; $9.25 \text{ kJ} \cdot \text{mol}^{-1}$, $-286.11 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $96.70 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$; $1.67 \text{ kJ} \cdot \text{mol}^{-1}$, $-308.74 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $96.03 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$; $5.05 \text{ kJ} \cdot \text{mol}^{-1}$, $-301.39 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $97.09 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$.

The values of ΔH° , ΔS° , and ΔG° at 298.15 K were $12.81 \text{ kJ} \cdot \text{mol}^{-1}$, $-275.41 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $94.92 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$; $9.31 \text{ kJ} \cdot \text{mol}^{-1}$, $-285.90 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $94.55 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$; $1.73 \text{ kJ} \cdot \text{mol}^{-1}$, $-308.53 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $93.72 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$; $5.11 \text{ kJ} \cdot \text{mol}^{-1}$, $-300.93 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $94.83 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$.

The values of k , E , and A of the title reactions were very low and the value of ΔS° was high. These facts showed that the title reactions easily took place in the temperature range $25\text{--}40^\circ\text{C}$.

3.3 Enthalpies of formation reactions for metal salts of NTO

The enthalpies of formation reactions for metal salts of NTO

Table 3 Values of n , $\ln k$, $\ln A$, E , ΔG° , ΔH° , and ΔS° of formation reaction of metal salts of NTO

T/K	n	$\ln(k/\text{s}^{-1})$	r	$E/(\text{kJ} \cdot \text{mol}^{-1})$	$\ln(A/\text{s}^{-1})$	r	$\Delta G^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H^\circ/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S^\circ/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	r
Li(NTO)·2H ₂ O										
298.15	0.984	-8.794	0.9989	15.29	-2.668	0.9989	94.92	12.81	-275.41	0.9989
303.15	1.002	-8.698	0.9987				96.30	12.77	-275.55	
308.15	1.128	-8.604	0.9985				97.68	12.73	-275.68	
313.15	1.020	-8.499	0.9999				99.06	12.69	-275.82	
Mean							96.99	12.75	-275.62	
Na(NTO)·H ₂ O										
298.15	1.030	-8.684	0.9989	11.79	-3.931	0.9991	94.55	9.31	-285.90	0.9985
303.15	1.150	-8.608	0.9969				95.98	9.27	-286.04	
308.15	1.154	-8.537	0.9999				97.41	9.23	-286.18	
313.15	1.276	-8.454	0.9985				98.85	9.19	-286.31	
Mean							96.70	9.25	-286.11	
Pb(NTO) ₂ ·H ₂ O										
298.15	0.664	-8.347	0.9995	4.21	-6.652	0.9995	93.72	1.73	-308.53	0.9989
303.15	0.996	-8.321	0.9989				95.26	1.69	-308.67	
308.15	0.911	-8.294	0.9981				96.81	1.65	-308.81	
313.15	1.360	-8.267	0.9985				98.34	1.61	-308.94	
Mean							96.03	1.67	-308.74	
Cu(NTO) ₂ ·2H ₂ O										
298.15	1.000	-8.799	0.9990	7.59	-5.737	0.9995	94.83	5.11	-300.93	0.9997
303.15	0.862	-8.751	0.9995				96.34	5.07	-301.07	
308.15	0.920	-8.700	0.9995				97.84	5.03	-301.21	
313.15	1.048	-8.653	0.9989				99.35	4.99	-301.34	
Mean							97.09	5.05	-301.39	

are listed in Table 4. From Table 4, one can see that the values of $\Delta_f H_m$ for metal salts of NTO are close at different temperatures.

3.4 Calculation of $\Delta_f H_m^0(\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f H_m^0(\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$

The formation reactions of alkali metal (Li and Na) salts of NTO could be represented as follows:

The following Eqs.(7) and (8) could represent the formation reactions of metal (Pb and Cu) salts of NTO:

According to Hess' law, the standard enthalpies of formation of $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$ (aq), $\Delta_f H_m^0(\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ and the standard enthalpies of formation of $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$ (aq), $\Delta_f H_m^0(\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ were calculated through Eqs.(9) and (10):

$$\begin{aligned} \Delta_f H_m^0(\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = & \frac{1}{2} \{ \Delta_f H_m^0[\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}(\text{cr}, 298.15 \text{ K})] + \\ & \Delta_f H_m^0[\text{Li}_2\text{SO}_4(\text{aq})] + 2\Delta_f H_m^0[\text{H}_2\text{O}(\text{l})] - \Delta_f H_m^0 - \\ & \Delta_f H_m^0[\text{CuSO}_4(\text{aq})] \} \end{aligned} \quad (9)$$

$$\begin{aligned} \Delta_f H_m^0(\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = & \frac{1}{2} \{ \Delta_f H_m^0[\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}(\text{cr}, 298.15 \text{ K})] + \\ & 2\Delta_f H_m^0[\text{NaNO}_3(\text{aq})] + \Delta_f H_m^0[\text{H}_2\text{O}(\text{l})] - \Delta_f H_m^0 - \end{aligned}$$

Table 4 Enthalpies of formation reactions for metal salts of NTO*

T/K	$-\Delta_f H_m^0/(\text{kJ} \cdot \text{mol}^{-1})$			
	$\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$	$\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$	$\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$	$\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$
298.15	39.22	37.85	1.41	11.34
	39.12	37.79	1.45	11.21
	39.08	37.61	1.50	11.29
	39.19	37.89	1.39	11.30
Mean	39.15±0.06	37.79±0.12	1.44±0.05	11.29±0.03
303.15	38.59	39.88	1.42	11.39
	38.67	39.65	1.41	11.41
	38.51	39.97	1.38	11.34
	38.48	39.81	1.47	11.46
Mean	38.56±0.13	39.83±0.14	1.42±0.04	11.40±0.05
308.15	35.91	36.88	1.37	11.01
	35.88	36.92	1.33	10.89
	35.79	36.98	1.40	10.92
	35.85	37.11	1.39	10.82
Mean	35.88±0.06	36.97±0.10	1.37±0.03	10.91±0.08
313.15	37.27	38.31	1.48	10.86
	37.33	38.20	1.42	10.67
	37.21	38.09	1.51	10.81
	37.38	38.27	1.49	10.71
Mean	37.30±0.07	38.22±0.10	1.48±0.02	10.76±0.09

*Uncertainty is twice the standard deviation of the mean, i.e., $2\sigma_{\text{mean}}$.

$$\Delta_f H_m^0[\text{Pb}(\text{NO}_3)_2(\text{aq})] \quad (10)$$

where, $\Delta_f H_m^0[\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}] = -(274.4 \pm 5.9) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0[\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}] = -(712.1 \pm 5.4) \text{ kJ} \cdot \text{mol}^{-1}$, taken from reference,²⁵ $\Delta_f H_m^0[\text{H}_2\text{O}(\text{l})] = -285.83 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0[\text{Pb}(\text{NO}_3)_2, \text{aq}] = -568.60 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0(\text{CuSO}_4, \text{aq}) = -844.50 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0(\text{Li}_2\text{SO}_4, \text{aq}) = -1446.19 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0(\text{NaNO}_3, \text{aq}) = -469.64 \text{ kJ} \cdot \text{mol}^{-1}$, taken from reference.²⁶

The following values are obtained:

$$\begin{aligned} \Delta_f H_m^0(\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) &= -(937.08 \pm 5.40) \text{ kJ} \cdot \text{mol}^{-1}, \\ \Delta_f H_m^0(\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) &= -(464.74 \pm 5.90) \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned}$$

4 Conclusions

(1) On the basis of experimental and calculated results, the reaction rates of the formation of $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$, $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ in the studied temperature range were found to be of the first order. The formation reactions of Li, Na, and Cu salts of NTO were exothermic, but the reaction of preparing Pb salt of NTO was endothermic.

(2) The enthalpies of reaction at 298.15, 303.15, 308.15, and 313.15 K were -39.12 , -38.59 , -35.88 , and $-37.27 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$; -37.79 , -39.88 , -36.98 , and $-38.20 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$; 1.45 , 1.42 , 1.37 , and $1.49 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$; -11.29 , -11.39 , -10.92 , and $-10.71 \text{ kJ} \cdot \text{mol}^{-1}$ for $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$.

(3) The activation energies of the formation reactions of $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$, $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ in the temperature range $25-40^\circ \text{C}$ were very low; and the enthalpies of the formation reactions of $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$, $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$, and $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ in our studied temperature range were low. The title reactions easily took place in the temperature range $25-40^\circ \text{C}$.

(4) $\Delta_f H_m^0(\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = -(937.08 \pm 5.40) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^0(\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = -(464.74 \pm 5.90) \text{ kJ} \cdot \text{mol}^{-1}$.

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