Journal of Thermal Analysis, Vol. 45 (1995) 79-86

STANDARD ENTHALPY OF FORMATION OF METAL (K, Ba, Li, Ca, Gd, Pb, Cu AND Zn) SALTS OF NTO

*Zihui Meng and Rongzu Hu**

Xian Modern Chemistry Research Institute, Xian 710061 Shaanxi, P. R. China

Abstract

From measurements of the enthalpy of solution of metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) in water, the standard enthalpies of formation of KNTO·H_2O, $Ba(NTO)_2$·$3H_2O$, LiNTO·$2H_2O$, $Ca(NTO)_2$·$4H_2O$ and $Gd(NTO)_3$·$7H_2O$ were determined as –(676.9±2.6), –(1627.0±2.5), –(966.6.3±2.2), –(1905.5±4.4) and –(3020.1±6.4) $kJ \cdot mol^{-1}$, respectively. From measurements of the enthalpy of precipitation of KNTO·H_2O crystal with $Pb(NO_3)_2$(aq), $CuSO_4$(aq) and $Zn(NO_3)_2$(aq), the standard enthalpies of formation of $Pb(NTO)_2$·H_2O, $Cu(NTO)_2$·$2H_2O$ and $Zn(NTO)_2$·H_2O were determined as –(247.4±5.9), –(712.1±5.4) and –(628.8±5.7) $kJ \cdot mol^{-1}$, respectively.

Keywords: enthalpy of formation, enthalpy of reaction, enthalpy of solution, microcalorimetry, NTO salts

Introduction

The use of certain metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) as energetic combustion catalysts in propellants has recently been proposed [1]. The standard enthalpies of formation of the silver, ammonium, sodium and potassium salts of NTO have been determined [2, 3]. The present paper reports the determination of the standard enthalpies of formation of the potassium salt monohydrate (KNTO·H_2O), the barium salt trihydrate ($Ba(NTO)_2$·$3H_2O$), the lithium salt dihydrate (LiNTO·$2H_2O$), the calcium salt tetrahydrate ($Ca(NTO)_2$·$4H_2O$), the gadolinium salt heptahydrate ($Gd(NTO)_3$·$7H_2O$), the lead salt monohydrate ($Pb(NTO)_2$·H_2O), the copper salt dihydrate ($Cu(NTO)_2$·$2H_2O$) and the zinc salt monohydrate ($Zn(NTO)_2$·H_2O) of NTO by means of solution/reaction calorimetry.

* To whom correspondence should be addressed.

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

Experimental

Materials

The $KNTO \cdot H_2O$, $Ba(NTO)_3 \cdot 3H_2O$, $LiNTO \cdot 2H_2O$, $Ca(NTO)_2 \cdot 4H_2O$, $Gd(NTO)_3 \cdot 7H_2O$, $Pb(NTO)_2 \cdot H_2O$, $Cu(NTO)_2 \cdot 2H_2O$ and $Zn(NTO)_2 \cdot H_2O$ used in this work were prepared and recrystallized according to reported methods [4].

The results of chemical analysis and elemental analysis showed that these salts had the expected compositions and were pure enough for calorimetric experiments.

All salts were sieved through a 160 mesh sifter before experiments.

The conductivity of the deionized water used in the experiments was 5.48×10^{-8} s·cm^{-1}.

0.02502 *M* $Pb(NO_3)_2$(aq), 0.05607 *M* $CuSO_4$(aq) and 0.05204 *M* $Zn(NO_3)_2$(aq) were prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (AR,>99%), $CuSO_4 \cdot 5H_2O$ (AR,>99%) and $Pb(NO_3)_2$ (GR,99.9%) in deionized water. All these reagents were commercial products of the Xian Chemical Reagent Factory.

Experimental equipment and conditions

All measurements were made with a Calvet microcalorimeter, type BT215 from SETARAM, France, and operated at (298.15±0.005) K as described previously [5].

The experimental precision and accuracy of enthalpies of solution were frequently checked by measurements of the enthalpies of solution of KCl(cr) in deionized water.

Results and discussion

Results on the enthalpies of solution of $M(NTO)_n \cdot mH_2O$(cr) (M=K, n=1, m=1; M=Ba, n=2, m=3; M=Li, n=1, m=2; M=Ca, n=2, m=4; M=Gd, n=3, m=7) in deionized water at 298.15 K are reported in Tables 1–5, where $\Delta_{sln}H_m^{\ominus}$ denotes the enthalpy of solution in water of the NTO salt, m is the mass of the NTO salt, and r is the molar ratio $n(H_2O)/n(M(NTO)_n \cdot mH_2O)$.

Results on the enthalpy $\Delta_r H_m^{\ominus}$ of precipitation of $KNTO \cdot H_2O$ with $Pb(NO_3)_2$(aq), $CuSO_4$(aq) and $Zn(NO_3)_2$(aq) at 298.15 K are reported in Tables 6–8, where m denotes the mass of $KNTO \cdot H_2O$ crystal.

Throughout this paper, the uncertainty intervals of the reported experimental results denote 99% confidence limits, calculated using Student's it-test with the appropriate number of degrees of freedom.

As the above salts were completely ionized in aqueous solution, and no solid residue was observed in the solution after calorimetry, the following equation holds:

$$M(NTO)_n{\cdot}mH_2O(cr)\xrightarrow{\Delta_{sln}H_m^\ominus} M^{n+}(aq,\infty) + nNTO^-(aq,\infty)+mH_2O(l) \quad (1)$$

The results for the solution reaction show a slight concentration dependence and the dilution of the final state in solution experiments; i.e. the values of r, is high enough to approximate closely to infinite dilution, and thus the following equation holds:

Table 1 Enthalpy of solution in water of $KNTO{\cdot}H_2O(cr)$ at 298.15 K

m /mg	r	$\Delta_{sln}H_m^\ominus$/kJ·mol^{-1}
7.284	13310	45.06
8.932	10800	43.61
9.147	10604	44.23
11.311	8539	44.68
12.403	7950	44.52
15.376	6292	45.32
16.601	5819	44.01
17.284	5589	44.01
20.176	4789	44.28
22.301	4340	43.78
25.505	3772	44.08
27.163	3554	44.94
29.778	3243	45.24
		Mean 44.41±0.48

$$\Delta_fH_m^\ominus(M(NTO)_n{\cdot}mH_2O,\ cr,\ 298.15\ K) = \Delta_fH_m^\ominus(M^{n+},\ aq,\ \infty) + n\Delta_fH_m^\ominus(NTO^-,\ aq,\ \infty) + m\Delta_fH_m^\ominus(H_2O,\ l) - \Delta_{sln}H_m^\ominus \quad (2)$$

By substituting the mean of the $\Delta_{sln}H_m^\ominus$ values in Tables 1 –5 and the reported values $\Delta_fH_m^\ominus(NTO^-,aq,\infty)=-(94.3\pm2.1)$ kJ·mol^{-1} [2], $\Delta_fH_m^\ominus$ $(H_2O,l)=-285.83$ kJ·mol^{-1}[6], $\Delta_fH_m^\ominus$ $(K^+,aq,\infty)=-252.38$ kJ·mol^{-1} [6], $\Delta_fH_m^\ominus$ $(Ba^{2+},aq,\infty)= -537.64$ kJ·mol^{-1} [6], $\Delta_fH_m^\ominus$ $(Li^+,aq,\infty=-278.48$ kJ·mol^{-1} [6], $\Delta_fH_m^\ominus$ $(Ca^{2+},aq,\ \infty=-542.83$ kJ·mol^{-1} [6], and $\Delta_fH_m^\ominus$ $(Gd^{3+},\ aq,\ \infty)=-686.18$ kJ·mol^{-1} [6], into Eq. (2), the following values were obtained:

$$\Delta_fH_m^\ominus(KNTO{\cdot}H_2O,\ cr,\ 298.15\ K)=-(676.9\pm2.6)\ kJ{\cdot}mol^{-1}$$

Table 2 Enthalpy of solution in water of $Ba(NTO)_2{\cdot}3H_2O(cr)$ at 298.15 K

m /mg	r	$\Delta_{sln}H_m^{\ominus}$/kJ·mol^{-1}
5.30	79638	43.65
6.594	66942	43.53
6.433	65137	43.21
9.312	47443	43.20
10.242	43033	43.01
12.176	36335	43.39
15.152	29026	42.91
15.388	28681	43.01
15.450	31764	44.00
		Mean 43.32±0.39

Table 3 Enthalpy of solution in water of $LiNTO{\cdot}2H_2O(cr)$ at 298.15 K

m /mg	r	$\Delta_{sln}H_m^{\ominus}$/kJ·mol^{-1}
2.534	26969	22.00
2.640	25936	22.00
4.791	16407	22.09
6.596	10560	22.17
6.892	9808	22.31
7.315	9225	22.16
8.740	7626	22.02
10.000	6696	22.12
10.041	6749	22.20
10.030	6684	22.30
11.022	6207	22.26
13.034	6135	22.14
10.970	6142	22.20
11.965	5686	22.25
11.954	5674	22.68
11.952	5697	22.02
		Mean 22.16±0.08

$$\Delta_f H_m^{\ominus}(Ba(NTO)_2{\cdot}3H_2O,cr,298.15\ K) = -(1627.0\pm2.5)\ kJ{\cdot}mol^{-1}$$

$$\Delta_f H_m^{\ominus}(LiNTO{\cdot}2H_2O,cr,298.15\ K) = -(966.6\pm2.2)\ kJ{\cdot}mol^{-1}$$

Table 4 Enthalpy of solution in water of $Ca(NTO)_2 \cdot 4H_2O(cr)$ at 298.15 K

m /mg	r	$\Delta_{sln}H_m^{\ominus}$/kJ·mol^{-1}
6.081	28548	31.24
9.442	19371	30.90
10.606	16359	30.84
16.935	10237	30.89
19.112	9075	30.33
21.536	8057	30.56
23.538	7361	31.07
27.060	6413	31.02
30.359	5713	30.43
35.360	4908	30.68
39.371	4406	30.73
45.352	3826	30.49
51.107	3394	30.70
55.288	3135	30.90
66.290	2616	30.30
		Mean 30.74±0.21

Table 5 Enthalpy of solution in water of $Gd(NTO)_3 \cdot 7H_2O(cr)$ at 298.15 K

m /mg	r	$\Delta_{sln}H_m^{\ominus}$/kJ·mol^{-1}
2.560	135832	50.20
5.841	59507	50.21
6.522	53316	50.11
6.738	51631	49.94
8.259	42280	50.33
8.700	39997	50.19
9.434	46843	50.29
13.229	27557	50.12
14.440	24123	50.03
		Mean 50.19±0.13

$$\Delta_f H_m^{\ominus}(Ca(NTO)_2 \cdot 4H_2O, cr, 298.15\ K) = -(1905.5 \pm 4.4)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m^{\ominus}(Gd(NTO)_3 \cdot 7H_2O, cr, 298.15\ K) = -(3020.1 \pm 6.4)\ kJ \cdot mol^{-1}$$

Table 6 Enthalpy of precipitation of $KNTO \cdot H_2O$(cr) with 0.02502 *M* $Pb(NO_3)_2$(aq) at 298.15 K

m /mg	$\Delta_r H^{\ominus}_{m1}$/kJ·mol^{-1}
4.381	83.45
5.482	82.37
7.064	83.36
8.248	81.86
9.567	82.61
11.500	81.81
12.740	82.34
12.794	82.45
19.179	81.61
	Mean 82.43±0.72

Table 7 Enthalpy of precipitation of $KNTO \cdot H_2O$(cr) with 0.05607 *M* $CuSO_4$(aq) at 298.15 K

m /mg	$\Delta_r H^{\ominus}_{m2}$/kJ·mol^{-1}
12.150	72.38
13.949	72.20
20.711	72.18
22.322	72.02
22.756	72.33
25.050	72.14
	Mean 72.20±0.21

Table 8 Enthalpy of precipitation of $KNTO \cdot H_2O$(cr) with 0.02504 *M* $Zn(NO_3)_2$(aq) at 298.15 K

m /mg	$\Delta_r H^{\ominus}_{m3}$/kJ·mol^{-1}
13.410	88.35
15.142	88.73
16.100	88.47
17.494	87.76
18.258	88.05
19.046	88.13
23.345	87.58
24.034	87.87
26.260	89.11
	Mean 88.30±0.53

According to precipitation reactions 3–5 for $KNTO\cdot H_2O(cr)$ with $Pb(NO_3)_2(aq)$, $CuSO_4(aq)$ and $Zn(NO_3)_2(aq)$:

$$Pb(NO_3)_2(aq) + 2KNTO\cdot H_2O(cr) \xrightarrow{\Delta_r H^{\ominus}_{m1}} Pb(NTO)_2\cdot H_2O\downarrow + 2KNO_3(aq) + H_2O(l) \qquad (3)$$

$$CuSO_4(aq) + 2KNTO\cdot H_2O(cr) \xrightarrow{\Delta_r H^{\ominus}_{m2}} Cu(NTO)_2\cdot 2H_2O\downarrow + K_2SO_4(aq) \qquad (4)$$

$$Zn(NO_3)_2(aq) + 2KNTO\cdot H_2O(cr) \xrightarrow{\Delta_r H^{\ominus}_{m3}} Zn(NTO)_2\cdot H_2O\downarrow + 2KNO_3(aq) + H_2O(l) \qquad (5)$$

and Eqs 6–8, deduced from reactions 3–5:

$$\Delta_f H^{\ominus}_m Pb(NTO)_2\cdot H_2O(cr) = \Delta_r H^{\ominus}_{m1} + \Delta_f H^{\ominus}_m Pb(NO_3)_2(aq) + 2\Delta_f H^{\ominus}_m KNTO\cdot H_2O(cr) - 2\Delta_f H^{\ominus}_m KNO_3(aq) - \Delta_f H^{\ominus}_m H_2O(l) \qquad (6)$$

$$\Delta_f H^{\ominus}_m Cu(NTO)_2\cdot 2H_2O(cr) = \Delta_r H^{\ominus}_{m2} + \Delta_f H^{\ominus}_m CuSO_4(aq) + 2\Delta_f H^{\ominus}_m KNTO\cdot H_2O(cr) - \Delta_f H^{\ominus}_m K_2SO_4(aq) \qquad (7)$$

$$\Delta_f H^{\ominus}_m Zn(NTO)_2\cdot H_2O(cr) = \Delta_r H^{\ominus}_{m3} + 2\Delta_f H^{\ominus}_m KNTO\cdot H_2O(cr) + \Delta_f H^{\ominus}_m Zn(NO_3)_2(aq) - 2\Delta_f H^{\ominus}_m KNO_3(aq) - \Delta_f H^{\ominus}_m H_2O(l) \qquad (8)$$

the enthalpies of formation of $Pb(NTO)_2\cdot H_2O(cr)$, $Cu(NTO)_2\cdot 2H_2O(cr)$ and $Zn(NTO)_2\cdot H_2O(cr)$ may be obtained from the values of $\Delta_r H^{\ominus}_m$ in Tables 6–8, $\Delta_f H^{\ominus}_m KNTO\cdot H_2O(cr) = -676.9\pm 2.6\ kJ\cdot mol^{-1}$, obtained in this work, $\Delta_f H^{\ominus}_m(KNO_3,aq,\infty) = -459.74\ kJ\cdot mol^{-1}$, $\Delta_f H^{\ominus}_m(H_2O,l) = -285.83\ kJ\cdot mol^{-1}$, $\Delta_f H^{\ominus}_m(CuSO_4,aq,\infty) = -844.50\ kJ\cdot mol^{-1}$, $\Delta_f H^{\ominus}_m(K_2SO_4,aq,\infty) = -1414.0\ kJ\cdot mol^{-1}$, $\Delta_f H^{\ominus}_m(Zn(NO_3)_2,aq,\infty) = -568.60\ kJ\cdot mol^{-1}$, taken from reference [6], and $\Delta_f H^{\ominus}_m(Pb(NO_3)_2,aq,\infty) = -181.3\ kJ\cdot mol^{-1}$, obtained from reaction (9):

$$Pb(NO_3)_2(cr) \xrightarrow{\Delta_{sln} H^{\ominus}_m} Pb(NO_3)_2(aq,\infty) \qquad (9)$$

and the values of $\Delta_f H^{\ominus}_m(Pb(NO_3)_2,cr) = -219.0\ kJ\cdot mol^{-1}$, taken from reference [7], and $\Delta_{sln} H^{\ominus}_m = 37.7\ kJ\cdot mol^{-1}$, from reference [8].

The following values are obtained:

$$\Delta_f H^{\ominus}_m(Pb(NTO)_2\cdot H_2O,cr,298.15\ K) = -(247.4\pm 5.9)\ kJ\cdot mol^{-1}$$

$$\Delta_f H^{\ominus}_m(Cu(NTO)_2\cdot 2H_2O,cr,298.15\ K) = -(712.1\pm 5.4)\ kJ\cdot mol^{-1}$$

$$\Delta_f H_m^{\ominus}(Zn(NTO)_2 \cdot H_2O, cr, 298.15\ K) = -(628.8 \pm 5.7)\ kJ \cdot mol^{-1}$$

References

1 Li Shangwen, Wang Jiangming, Fu Xiayun and Zhou Jihua, Energetic Materials, 1 (1993) 22 (in Chinese).
2 A. Finch, P. J. Gardner, A. J. Head and H. S. Majdi, J. Chem. Thermodynamics, 23 (1991) 1169.
3 A. Finch, P. J. Gardner, A. J. Head and H. S. Majdi, Thermochim. Acta, 213 (1993) 17.
4 Zhang Tonglai, Hu Rongzu and Li Fuping, Energetic Materials, 1 (1993) 827 (in Chinese).
5 Hu Rongzu, Liang Yanjun and Yang Zhengquan, Chemical Engineering, 4 (1987) 74 (in Chinese).
6 R. C. Weast, CRC Handbook of Chemistry and Physics, 63rd edition, CRC press Inc., Boca Raton, Florida 1982–1983, D52–95.
7 J. A. Dean, Lange's Handbook of Chemistry 12th, McGraw Hill Book Company, New York 1978, p. 9–26.
8 J. G. Stark and H. G. Wallace; Chemistry Data Book (SI edition), John Murray, 50 Albermarle Street, London 1975, p. 68.

Zusammenfassung — Ausgehend von den Lösungsenthalpien der Metallsalze von 3-Nitro-1,2,4-Triazol-5-on (NTO) in Wasser wurden die Standard-Bildungsenthalpien von $KNTO \cdot H_2O$, $Ba(NTO)_2 \cdot 3H_2O$, $LiNTO \cdot 2H_2O$, $Ca(NTO)_2 \cdot 4H2O$ und $Gd(NTO)_3 \cdot 7H_2O$ mit $-(676.9 \pm 2.6)$, $-(1627.0 \pm 2.5)$, $-(966.6 \pm 2.2)$, $-(1905.5 \pm 4.4)$ und $-(3020.1 \pm 6.4)$ kJ/mol ermittelt. Aus Messungen der Präzipitationsenthalpie von $KNTO \cdot H_2O$-Kristallen mit $Pb(NO_3)_2(aq)$, $CuSO_4(aq)$ und $Zn(NO_3)_2(aq)$ wurden die Standard-Bildungsenthalpien von $Pb(NTO)_2 \cdot H_2O$, $Cu(NTO)_2 \cdot 2H_2O$ und von $Zn(NTO)_2 \cdot H_2O$ mit $-(247.4 \pm 5.9)$, $-(712.1 \pm 5.4)$ und mit $-(628.8 \pm 5.7)$ kJ/mol ermittelt.