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Thermochemical properties of 2,6-diamino-3,5-dinitropyrazine-1-oxide in dimethyl sulfoxide and *N*-methyl pyrrolidone

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Abstract The molar enthalpies of dissolution for 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) in dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) were measured using a RD496-2000 Calvet microcalorimeter at 298.15 K under atmospheric pressure. Empirical formulae for the calculation of the molar enthalpies of dissolution ($\Delta_{\text{diss}}H$), relative partial molar enthalpies ($\Delta_{\text{diss}}H_{\text{partial}}$) and relative apparent molar enthalpies ($\Delta_{\text{diss}}H_{\text{apparent}}$) were obtained from the experimental data of the dissolution processes of LLM-105 in DMSO or NMP. Furthermore, the corresponding kinetic equations describing the two dissolution processes were $\mathrm{d}\alpha/\mathrm{d}t = 10^{-2.37}(1-\alpha)^{0.47}$ for the dissolution of LLM-105 in DMSO, and $\mathrm{d}\alpha/\mathrm{d}t = 10^{-2.38}(1-\alpha)^{0.42}$ for the dissolution of LLM-105 in NMP.

Keywords 2,6-Diamino-3,5-dinitropyrazine-1-oxide · Microcalorimeter · Dimethyl sulfoxide · *N*-Methyl pyrrolidone · Dissolution · Kinetics

Introduction

The development of new energetic materials continues to focus on the synthesis of new heterocycles with high density, high heat of formation and good oxygen balance. These materials have been shown to be useful as high explosives, components of propellants and gas generators [1–5]. In 1995, 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) was synthesized for the first time [6]. It was found that the predicted power was 125 % of the extremely insensitive explosive 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), 81 % of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [7, 8], and it was a thermally stable ($T_p = 342$ °C (DSC)), relatively insensitive energetic material ($H_{50} = 117$ cm). The energy content, power and thermal stability of LLM-105 make it very promising for several applications, including insensitive boosters and detonators.

The synthesis, properties and thermal behavior of LLM-105 have been reported widely [9–14], but the dissolution properties of LLM-105 in different solvents have never been investigated. The aim of this work is to study the dissolution processes of LLM-105 in DMSO and NMP intensively. At the same time, the kinetic equations of the two dissolution processes and the enthalpies of dissolution are obtained, respectively, which will be useful for purification of LLM-105 in production, and can provide valuable information for its applications in the propellant and explosive.

Experimental

Materials

The LLM-105 used in the experiment was prepared and purified by Xi'an Modern Chemistry Research Institute [15]. ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 9.064, 8.784 (d, 2H, NH); IR (KBr, υ/cm^{-1}): 3430, 3340, 3275, 3225, 1609, 1557, 1486, 1374, 1334, 1238, 1062, 885, 810, 711; Elemental anal. (%) calcd. for $C_4H_4N_6O_5$: C 22.22, H 1.48, N 38.89; found: C 22.57, H 1.45, N 38.65. Its purity was more than 99.6 %. The structure of LLM-105 is shown in Scheme 1. The sample was stored under vacuum before the

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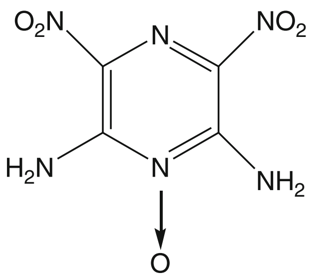

Scheme 1 Structure of LLM-105

experimental measurements. Both DMSO ($\rho = 1.098$–1.102 g cm^{-3}) and NMP ($\rho = 1.029$–1.035 g cm^{-3}) used as solvents were of analytical reagent grade, and their purities were higher than 99.4 %. Deionized water with an electrical conductivity of 0.8×10^{-4}–1.2×10^{-4} S m^{-1} used in the experiments was obtained by purification two times via a sub-boiling distillation device.

Equipment and conditions

All the measurement experiments were performed on a RD496-2000 Calvet microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., Ltd.), which had a sensitivity of 66.5 μV mW^{-1} at 298.15 K. The microcalorimeter was calibrated by the Joule effect, and the calibration was repeated after each experiment. The enthalpy of dissolution of KCl (spectrum purity) in distilled water measured on a RD496-2000 Calvet microcalorimeter at 298.15 K was 17.234 ± 0.041 kJ mol^{-1}, and the relative error was <0.04 % compared with the literature value 17.241 ± 0.018 kJ mol^{-1} [16]. This showed that the device for measuring the enthalpies used in this work was reliable. The enthalpies of dissolution were measured at 298.15 ± 0.005 K.

Table 1 Enthalpies of dissolution of LLM-105 in DMSO

$a \times 10^5$/mol	$b \times 10^2$/mol kg^{-1}	$\Delta_{\text{diss}}H$/kJ mol^{-1}	
		Experimental	Calculated
0.6204	0.2820	5.7740	5.7801
1.5231	0.6923	4.5137	4.4763
2.5370	1.1532	3.3665	3.4291
3.8380	1.7445	2.4409	2.3596
5.3935	2.4516	1.2684	1.2987

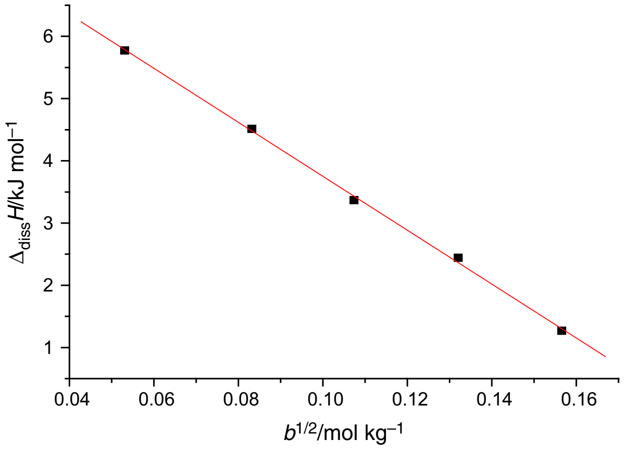

Fig. 1 Relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ of LLM-105 in DMSO

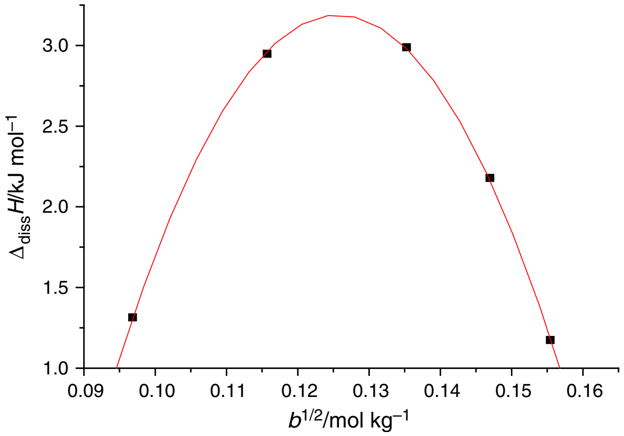

Fig. 2 Relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ of LLM-105 in NMP

Table 2 Enthalpies of dissolution of LLM-105 in NMP

$a \times 10^5$/mol	$b \times 10^2$/mol kg^{-1}	$\Delta_{\text{diss}}H$/kJ mol^{-1}		$\Delta_{\text{diss}}H_{\text{apparent}}$/kJ mol^{-1}	$\Delta_{\text{diss}}H_{\text{partial}}$/kJ mol^{-1}
		Experimental	Calculated		
1.9352	0.9376	1.3151	1.3074	33.8274	40.1417
2.7639	1.3391	2.9484	2.9643	35.4843	38.0881
3.7778	1.8303	2.9883	2.9791	35.4991	32.5570
4.4583	2.1601	2.1791	2.1624	34.6825	27.6046
4.9861	2.4158	1.1745	1.1863	33.7063	23.2497

Table 3 Original data of the dissolution process of LLM-105 in DMSO at 298.15 K

$m_{\text{LLM-105}}$/g	m_{DMSO}/g	t/s	$-(\mathrm{d}H/\mathrm{d}t)_i$/mJ s^{-1}	$(H/H_\infty)_i$	$-H_\infty$/kJ mol^{-1}
0.00134	2.2	240	0.18444	0.4270	5.7681
		300	0.16953	0.5580	
		360	0.15192	0.6676	
		420	0.13175	0.7544	
		480	0.11326	0.8218	
		540	0.09918	0.8733	
		600	0.08325	0.9124	
		660	0.07217	0.9413	
0.00329	2.2	240	0.24472	0.4471	4.5216
		300	0.21368	0.5864	
		360	0.18256	0.6971	
		420	0.15610	0.7822	
		480	0.13500	0.8459	
		540	0.11295	0.8932	
		600	0.09528	0.9279	
		660	0.07998	0.9530	
0.00548	2.2	240	0.26806	0.3038	3.3665
		300	0.24127	0.4497	
		360	0.21739	0.5808	
		420	0.18884	0.6902	
		480	0.16245	0.7769	
		540	0.13209	0.8435	
		600	0.11365	0.8927	
		660	0.09330	0.9284	
0.00829	2.2	240	0.19807	0.2823	2.4527
		300	0.17849	0.3963	
		360	0.16229	0.4995	
		420	0.14522	0.5899	
		480	0.13205	0.6674	
		540	0.11612	0.7332	
		600	0.10475	0.7885	
		660	0.09167	0.8346	
0.01165	2.2	240	0.22318	0.4344	1.2779
		300	0.20078	0.5490	
		360	0.18027	0.6423	
		420	0.16063	0.7175	
		480	0.14319	0.7779	
		540	0.12885	0.8265	
		600	0.11440	0.8659	
		660	0.10151	0.8978	

Results and discussion

Thermochemical behaviors of the dissolution of LLM-105 in DMSO and NMP

The proper molar sample of LLM-105 was, respectively, dissolved in DMSO and NMP at 298.15 K in order to form solutions. The molar enthalpy of the dissolution ($\Delta_{\text{diss}}H$) was detected on a RD496-2000 Calvet microcalorimeter. Each process was repeated three times to ensure the precision of the data [17–19]. The dissolution of LLM-105 in DMSO and NMP were all endothermic processes. The thermochemical data obtained, $\Delta_{\text{diss}}H$, b (the molality of LLM-105), $\Delta_{\text{diss}}H_{\text{partial}}$ (the relative partial molar enthalpy

Table 4 Original data of the dissolution process of LLM-105 in NMP at 298.15 K

$m_{\text{LLM-105}}$/g	m_{NMP}/g	t/s	$-(\mathrm{d}H/\mathrm{d}t)_{\mathrm{i}}$/mJ s^{-1}	$(H/H_{\infty})_{\mathrm{i}}$	$-H_{\infty}$/kJ mol^{-1}
0.00418	2.064	300	0.13009	0.4607	1.3246
		350	0.11987	0.5617	
		400	0.11125	0.6522	
		450	0.10043	0.7303	
		500	0.08904	0.7963	
		550	0.07746	0.8507	
		600	0.06666	0.8944	
		650	0.05811	0.9282	
0.00597	2.064	250	0.22641	0.4143	2.9395
		300	0.20807	0.5350	
		350	0.18568	0.6394	
		400	0.16176	0.7254	
		450	0.14065	0.7942	
		500	0.12415	0.8484	
		550	0.11052	0.8906	
		600	0.09201	0.9230	2.9963
0.00816	2.064	200	0.35135	0.4155	
		250	0.31530	0.5452	
		300	0.27817	0.6513	
		350	0.24684	0.7356	
		400	0.22034	0.8011	
		450	0.19642	0.8513	
		500	0.17893	0.8896	
		550	0.15461	0.9188	
0.00963	2.064	200	0.26907	0.3803	2.1683
		250	0.24569	0.5056	
		300	0.21941	0.6124	
		350	0.19426	0.7001	
		400	0.17371	0.7703	
		450	0.15662	0.8258	
		500	0.14033	0.8695	
		550	0.12299	0.9038	
0.01077	2.064	200	0.19613	0.3367	1.1825
		250	0.17933	0.4623	
		300	0.16119	0.5728	
		350	0.14626	0.6657	
		400	0.13143	0.7411	
		450	0.11858	0.8013	
		500	0.10634	0.8496	
		550	0.09343	0.8880	

of dissolution) and $\Delta_{\text{diss}}H_{\text{apparent}}$ (the relative apparent molar enthalpy of dissolution) are listed in Tables 1 and 2.

With the help of the values of b and $\Delta_{\text{diss}}H$ in Table 1, the empirical formula of enthalpy for the dissolution processes of LLM-105 in DMSO describing the b *vs.* $\Delta_{\text{diss}}H$ relation is obtained as

$$\Delta_{\text{diss}}H = 8.08 - 43.31b^{1/2} \tag{1}$$

According to the values of b and $\Delta_{\text{diss}}H$ in Table 2, the empirical formula of enthalpy for the dissolution processes of LLM-105 in NMP describing the b versus $\Delta_{\text{diss}}H$ relation is also obtained as

$$\Delta_{\text{diss}}H = -32.52 + 568.28b^{1/2} - 2260.98b \tag{2}$$

The empirical formula of relative molar enthalpy and relative partial molar enthalpy calculated by Eq. 2 are, respectively,

$$\begin{aligned}\Delta_{\text{diss}}H_{\text{apparent}} &= \Delta_{\text{diss}}H(b=b) - \Delta_{\text{diss}}H(b=0)\\ &= 568.28b^{1/2} - 2260.98b\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta_{\text{diss}}H_{\text{partial}} &= b\left(\frac{\partial \Delta_{\text{diss}}H}{\partial b}\right) + \Delta_{\text{diss}}H_{\text{apparent}}\\ &= 852.42b^{1/2} - 4521.96b\end{aligned} \tag{4}$$

From Tables 1 and 2, we can see that the molality of the solution b can affect the values of $\Delta_{\text{diss}}H$, the calculated $\Delta_{\text{diss}}H_{\text{apparent}}$ and $\Delta_{\text{diss}}H_{\text{partial}}$. The $\Delta_{\text{diss}}H$, $\Delta_{\text{diss}}H_{\text{apparent}}$ and $\Delta_{\text{diss}}H_{\text{partial}}$ change with the values of b during the dissolution processes of LLM-105 in DMSO and NMP. We can also find the relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ for the dissolution processes of LLM-105 in DMSO is linear equation from Fig. 1, and at the same time the relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ for the dissolution processes of LLM-105 in NMP is quadratic equation from Fig. 2.

Kinetics of dissolution processes of LLM-105 in DMSO and NMP

Equations 5 and 6 were chosen as the model functions for describing the dissolution of LLM-105 in DMSO or NMP [20, 21].

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{5}$$

$$f(\alpha) = (1-\alpha)^{n} \tag{6}$$

Combining Eqs. 5 and 6 yields

$$\frac{d\alpha}{dt} = k(1-\alpha)^{n} \tag{7}$$

Substituting $\alpha = H/H_\infty$ into Eq. 7, we get

$$\ln\left[\frac{1}{H_\infty}\left(\frac{dH}{dt}\right)_{i}\right] = \ln k + n\ln\left[1-\left(\frac{H}{H_\infty}\right)_{i}\right] \tag{8}$$

where $i = 1, 2, \ldots L$

In these equations, α is the conversion degree, $f(\alpha)$ is the kinetic model function, H represents the enthalpy at time of t, i is any time during the process, H_∞ is the enthalpy of the whole process, k is the rate constant of LLM-105 dissolved in DMSO or NMP, n is the reaction order and L is counting number.

The data needed for Eq. 8 are summarized in Tables 3 and 4. Substituting the original data in Tables 3 and 4, $-(dH/dt)_i$, $(H/H_\infty)_i$, H_∞, $i = 1, 2, \ldots, L$, into the kinetic Eq. 8 yields the values of n and ln$k$ that are listed in Table 5.

Table 5 Values of n, ln$k$ and the correlative coefficient r for the dissolution process at 298.15 K

Solvent	n	ln$k$	r
DMSO	0.424	−5.015	0.9998
	0.455	−5.379	0.9999
	0.468	−5.580	0.9993
	0.519	−5.997	0.9997
	0.461	−5.465	0.9996
Mean	0.465	−5.487	
NMP	0.407	−5.005	0.9997
	0.439	−5.646	0.9996
	0.413	−5.568	0.9998
	0.416	−5.697	0.9999
	0.411	−5.537	0.9998
Mean	0.417	−5.491	

Substituting the values of n and k in Table 5 into Eq. 7, we can get

$$\frac{d\alpha}{dt} = 10^{-2.37}(1-\alpha)^{0.47} \tag{9}$$

for the dissolution process of LLM-105 in DMSO, and

$$\frac{d\alpha}{dt} = 10^{-2.38}(1-\alpha)^{0.42} \tag{10}$$

for the dissolution process of LLM-105 in NMP.

The values of k indicate that the reaction of LLM-105 dissolved in DMSO and NMP are same; the reaction orders can also be considered to be similar.

Conclusions

1. The dissolution processes of LLM-105 in DMSO and NMP were investigated by RD496-2000 Calvet microcalorimeter at 298.15 K. The enthalpies can be regarded as the corresponding enthalpies at infinite dilution because of the very low molalities.
2. The relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ for LLM-105 dissolved in DMSO is linear equation, while the relationship between $\Delta_{\text{diss}}H$ and $b^{1/2}$ for the dissolution processes of LLM-105 dissolved in NMP is quadratic equation. This means that the molality (b) is one of the important factors that influences the dissolution process.
3. The kinetic equations of dissolution processes of LLM-105 are $d\alpha/dt = 10^{-2.37}(1-\alpha)^{0.47}$ in DMSO, and $d\alpha/dt = 10^{-2.38}(1-\alpha)^{0.42}$ in NMP, which indicate that the reaction rates and reaction orders of LLM-105 dissolved in DMSO and NMP are similar.

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