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Thermochemical properties of 1,1-diamino-2,2-dinitroethylene (FOX-7) in dimethyl sulfoxide (DMSO)

Xing Xiao-Ling, Xue Liang, Zhao Feng-Qi*, Gao Hong-Xu, Hu Rong-Zu

Propellant and Explosive Combustion Key Lab of Science and Technology for National Defence, Xi'an Modern Chemistry Research Institute, Xi'an City 710065, China

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ABSTRACT

The enthalpy of dissolution of 1,1-diamino-2,2-dinitroethylene (FOX-7) in DMSO was measured by means of a RD496-2000 Calvet microcalorimeter at 298.15 K. Empirical formulae for the calculation of the enthalpy of dissolution ($\Delta_{\mathrm{diss}}H$), relative partial molar enthalpy ($\Delta_{\mathrm{diss}}H_{\mathrm{partial}}$) and relative apparent molar enthalpy ($\Delta_{\mathrm{diss}}H_{\mathrm{apparent}}$) were obtained from the experimental data of the enthalpies of dissolution of FOX-7 in dimethyl sulfoxide (DMSO). The dilution/crystallization kinetic behavior of FOX-7 in DMSO/water system was investigated and the kinetic equation describing the dilution/crystallization process was presented.

1. Introduction

FOX-7 (1,1-diamino-2,2-dinitroethylene) is a new nitramine explosive and an energetic ingredient of solid propellant [1,2]. Since the successful synthesis of FOX-7, its good performances have attracted people's much attention in the field of energetic materials [3,4]. Compared with RDX, the sensitivity of FOX-7 is lower than that of 1,3,5-trinitro-1,2,4-triazacyclohexane (RDX), but its energy level is close to that of RDX. FOX-7 is compatible with usual additives used for energetic materials. It can be expected that FOX-7 has a good potential application in the future.

Quite lots of properties of FOX-7 have been measured and studied [5–7], including density, reactivity, thermal stability, compatibility, sensitivity, specific heat capacity and so on. The single crystal of FOX-7 was also prepared and detected for phase transitions [8]. But the particular properties of its solution have never been reported so far. The aim of this work is to study the thermochemical properties of FOX-7 in DMSO and the dilution/crystallization kinetics of FOX-7 in DMSO/water system. This is useful in studying its industrial crystallization process.

2. Experimental

2.1. Materials

FOX-7 used as crystalloid was prepared by Xi'an Modern Chemistry Research Institute, its purity was more than 99.5%. DMSO (m.p. 18–20; $d_4^{20} = 1.098\text{–}1.102$) used as solvent was of analytical purity. Distilled water was twice distilled by ourselves in laboratory.

2.2. Equipment and conditions

All measurements were made using a RD496-2000 Calvet microcalorimeter. The enthalpy of dissolution of KCl (spectrum purity) in distilled water measured by RD496-2000 Calvet microcalorimeter at 298.15 K was 17.234 kJ mol^{-1}, and the relative error was less than 0.04% compared with the literature value 17.24 kJ mol^{-1}. This showed that the device of measuring the enthalpy used in this work was reliable. The enthalpies of dissolution were measured at 298.15 ± 0.005 K and the dilution/crystallization processes was operated at four different temperature. The heat flow curves obtained under the same conditions overlap with each other, indicating that the reproducibility of test was satisfactory.

3. Results and discussion

3.1. Enthalpy of dissolution of FOX-7 in DMSO

The experimental and calculated values of enthalpy of dissolution [9] in DMSO for FOX-7 are given in Table 1 and the calculated relative apparent molar enthalpy and relative partial molar enthalpy of FOX-7 are also given in Table 1. In Table 1, b represents the concentration of the solution after FOX-7 dissolved in DMSO.

With the help of the values of b and $\Delta_{\mathrm{diss}}H$ in Table 1, the empirical formula of enthalpy describing the b vs. $\Delta_{\mathrm{diss}}H$ relation

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* Corresponding author. Tel.: +86 29 88291663.
E-mail address: npecc@163.com (F.-Q. Zhao).

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Table 1
The enthalpies of dissolution of FOX-7 in DMSO.

$b \times 10^2$ (mol kg^{-1})	$b^{1/2}$	$\Delta_{\rm diss}H$ (kJ mol^{-1})		$\Delta_{\rm diss}H_{\rm partial}$ (kJ mol^{-1})	$\Delta_{\rm diss}H_{\rm apparent}$ (kJ mol^{-1})
		Found	Calculated		
2.14	0.146	−8.64	−8.58	−18.04	−16.48
2.50	0.158	−8.81	−8.80	−17.28	−16.66
3.00	0.173	−8.83	−8.79	−15.71	−16.60
3.18	0.178	−8.73	−8.72	−15.04	−16.56
3.68	0.192	−8.38	−8.37	−12.98	−16.22

is obtained:

$$\Delta_{\rm diss}H = 8.2146 - 207.343b^{1/2} + 629.7194b \qquad (1)$$

The empirical formulae of relative apparent molar enthalpy and relative partial molar enthalpy calculated by Eq. (1) are

$$\begin{aligned}\Delta_{\rm diss}H_{\rm apparent} &= \Delta_{\rm diss}H(b=b) - \Delta_{diss}H(b=0)\\ &= -207.343b^{1/2} + 629.7194b \qquad (2)\end{aligned}$$

$$\begin{aligned}\Delta_{\rm diss}H_{\rm partial} &= b\left(\frac{\partial \Delta_{\rm diss}H}{\partial b}\right) - \Delta_{\rm diss}H_{\rm apparent}\\ &= 1259.44b - 311.0145b^{1/2} \qquad (3)\end{aligned}$$

respectively.

3.2. The kinetics of dissolution process of FOX-7 in DMSO

The proper molar crystalloid of FOX-7 was dissolved in DMSO at 298.15 K in order to form solution. The enthalpy of the process was detected by the RD496-2000 Calvet microcalorimeter. The entire process was repeated several times.

The kinetic equation describing the dissolution of FOX-7 in DMSO is Eq. (4) and Eq. (5) [10] is chosen as the model function describing the process:

$$\frac{{\rm d}\alpha}{{\rm d}t} = kf(\alpha) \qquad (4)$$

$$f(\alpha) = (1-\alpha)^n \qquad (5)$$

Combining Eqs. (4) and (5), yields:

$$\frac{{\rm d}\alpha}{{\rm d}t} = k(1-\alpha)^n \qquad (6)$$

Substituting $\alpha = H/H_\infty$ into Eq. (6), we get:

$$\ln\left[\frac{1}{H_\infty}\left(\frac{{\rm d}H}{{\rm d}t}\right)_i\right] = \ln k + n\ln\left[1-\left(\frac{H}{H_\infty}\right)_i\right] \quad i = 1, 2, \ldots, L \qquad (7)$$

In these equations, α is the conversion degree, H represents the enthalpy at time of t, i is the any time during the process, H_∞ is the enthalpy of the whole process, k is the rate of FOX-7 dissolved in DMSO, and n is the reaction order.

The data needed for Eq. (7) is summarized in Table 2.

By putting the original data in Table 2, $-({\rm d}H/{\rm d}t)_i$, $(H/H_\infty)_i$, H_∞, $i = 1,2,\ldots,L$, into kinetic Eq. (7), the values of n and $\ln k$ listed in Table 3 are obtained.

The kinetic equation describing the dissolution of FOX-7 in DMSO at 298.15 K may be expressed as

$$\frac{{\rm d}\alpha}{{\rm d}t} = 1.12 \times 10^{-8}(1-\alpha)^{0.7} \qquad (8)$$

Table 2
The original data of the dissolution process of FOX-7 in DMSO at 298.15 K.

m (g)	$m_{\rm DMSO}$ (g)	t (s)	$-({\rm d}H/{\rm d}t)_i$ (mJ s^{-1})	$(H/H_0)_i$	$-H_\infty$ (kJ mol^{-1})
0.0069	2.20	40	0.0538	0.1055	8.58
		80	0.0601	0.1935	
		120	0.0605	0.2863	
		160	0.0575	0.3770	
		200	0.0527	0.4616	
		240	0.0473	0.5383	
		280	0.0419	0.6066	
		320	0.0368	0.6670	
		360	0.0321	0.7197	
		400	0.0279	0.7656	
		440	0.0241	0.8054	
		480	0.0209	0.8399	
		520	0.0180	0.8696	
		560	0.0155	0.8952	
		600	0.0134	0.9173	
		640	0.0115	0.9363	
		680	0.0099	0.9527	
		720	0.0085	0.9667	
0.0082	2.20	40	0.0674	0.2451	8.81
		80	0.0662	0.3295	
		120	0.0626	0.4109	
		160	0.0577	0.4869	
		200	0.0522	0.5562	
		240	0.0467	0.6186	
		280	0.0414	0.6742	
		320	0.0365	0.7232	
		360	0.0319	0.7664	
		400	0.0279	0.8041	
		440	0.0242	0.8369	
		480	0.0210	0.8654	
		520	0.0182	0.8900	
		560	0.0157	0.9114	
		600	0.0136	0.9299	
		640	0.0117	0.9458	
		680	0.0101	0.9595	
		720	0.0087	0.9713	
0.0097	2.20	40	0.0751	0.3295	8.79
		80	0.0707	0.4109	
		120	0.0650	0.4869	
		160	0.0589	0.5562	
		200	0.0529	0.6186	
		240	0.0472	0.6742	
		280	0.0420	0.7232	
		320	0.0371	0.7664	
		360	0.0327	0.8041	
		400	0.0287	0.8369	
		440	0.0251	0.8654	
		480	0.0219	0.8900	
		520	0.0189	0.9114	
		560	0.0164	0.9299	
		600	0.0141	0.9458	
		640	0.0122	0.9595	
		680	0.0105	0.9713	
		720	0.0091	0.9815	
0.0104	2.20	40	0.0864	0.2555	8.72
		80	0.0831	0.3406	
		120	0.0775	0.4212	
		160	0.0707	0.4954	
		200	0.0636	0.5627	
		240	0.0566	0.6228	
		280	0.0499	0.6761	
		320	0.0439	0.7231	
		360	0.0383	0.7642	
		400	0.0334	0.8001	
		440	0.0290	0.8302	
		480	0.0252	0.8585	
		520	0.0219	0.8821	
		560	0.0189	0.9025	
		600	0.0164	0.9201	
		640	0.0141	0.9354	
		680	0.0123	0.9486	
		720	0.0107	0.9601	
0.0120	2.20	40	0.0692	0.0670	8.37
		80	0.0831	0.1366	
		120	0.0876	0.2143	

Table 2 (*Continued*)

m (g)	m_{DMSO} (g)	t (s)	$-(\mathrm{d}H/\mathrm{d}t)_i$ (mJ s^{-1})	$(H/H_0)_i$	$-H_\infty$ (kJ mol^{-1})
		160	0.0867	0.2936	
		200	0.0824	0.3703	
		240	0.0764	0.4423	
		280	0.0697	0.5085	
		320	0.0631	0.5687	
		360	0.0567	0.6229	
		400	0.0509	0.6716	
		440	0.0454	0.7152	
		480	0.0405	0.7547	
		520	0.0360	0.7887	
		560	0.0319	0.8195	
		600	0.0282	0.8467	
		640	0.0250	0.8708	
		680	0.0220	0.8921	
		720	0.0194	0.9109	

Table 3
The values of n, $\ln k$ and the correlative coefficient r for the dissolution process at 298.15 K.

n	$\ln k$	r
0.6722	−18.556	0.996
0.7056	−18.401	0.997
0.6749	−18.294	0.998
0.7444	−18.164	0.993
0.6912	−18.157	0.995

3.3. *The dilution/crystallization kinetic behavior of FOX-7 in DMSO/water system*

The crystal of FOX-7 developed from the solution can be express as

$$\mathrm{A(aq)} - \mathrm{A(s)} + Q \tag{9}$$

$$\begin{array}{lllll} t=0 & c_0 & 0 & & 0 \\ t=t & c & m, \alpha & & H \\ t=\infty & c_\infty & m_\infty, \alpha_\infty = 1 & & H_\infty \end{array}$$

where Q is the heat produced during a certain time t, c stands for the concentration of FOX-7 solution at time of t, m is the mass of the already formed crystal, α is the conversion degree, H is the enthalpy at time t. When $t = 0$, then $c = c_0$, $m = 0$, $H = 0$ and when $t = \infty$, the values of $m = m_\infty$, $\alpha = \alpha_\infty = 1$, $H = H_\infty$ are got.

The distilled water was added to the FOX-7-DMSO system with a fast speed at different temperatures, and the dilution/crystallization enthalpy was measured using the microcalorimeter mentioned above. The experiment conditions are listed as Table 4, the serial number is from 1 to 4.

The original data of the dilution/crystallization process at different temperature are shown in Table 5.

Based on Burton–Cabrera–Frank dislocation theory [11], for relatively high super saturations, the rate of crystal growth ($\mathrm{d}m/\mathrm{d}t$) can be written as follows:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = k m_\infty (c - c_\infty) \tag{10}$$

Table 4
The experiment conditions for the dilution/crystallization process of FOX-7 in DMSO–H_2O system.

Number	T (K)	m_{sample} (g)	m_{DMSO} (g)	m_{water} (g)
1	301.15	0.0104	1.2101	1.0003
2	308.15	0.0136	1.2112	1.0008
3	313.15	0.0102	1.2098	1.0010
4	318.15	0.0115	1.2106	1.0015

Table 5
The original data for the dilution/crystallization process of FOX-7 in DMSO–H_2O system.

t (s)	$(\mathrm{d}H/\mathrm{d}t)_i$ (mJ s^{-1})			
	No. 1	No. 2	No. 3	No. 4
200		0.2100	0.1875	0.6174
230	0.1273	0.1987	0.1796	0.5849
260	0.1224	0.1862	0.1712	0.5502
290	0.1171	0.1727	0.1629	0.5143
320	0.1113	0.1597	0.1544	0.4787
350	0.1053	0.1475	0.1460	0.4410
380	0.0992	0.1365	0.1377	0.4046
410	0.0931	0.1261	0.1297	0.3720
440	0.0873	0.1165	0.1219	0.3372
470	0.0814	0.1074	0.1141	0.3056
500	0.0758	0.0989	0.1068	0.2758
530	0.0704	0.0909	0.0997	0.2482
560	0.0652	0.0832	0.0930	0.2223
590	0.0604	0.0760	0.0865	0.1979
620	0.0558	0.0693	0.0803	0.1756
650	0.0515	0.0629	0.0745	0.1548
680	0.0474	0.0570	0.0690	0.1363
710	0.0435	0.0514	0.0638	0.0885
740	0.0400			

When $c \gg c_\infty$, Eqs. (11) and (12) are obtained one after the other:

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\mathrm{d}m}{\mathrm{d}t}\left(\frac{H_\infty}{m_\infty}\right) = kH_\infty c_0\left(1 - \frac{H}{H_\infty}\right) = k_2\left(1 - \frac{H}{H_\infty}\right) + a \tag{11}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{k_2(1 - H/H_\infty) + a}{H_\infty/m_\infty} = km_\infty(c - c_\infty) + b \tag{12}$$

where k and k_2 are the reactive velocity constants of the dilution/crystallization process of FOX-7 in DMSO–H_2O system, a and b are constants.

The kinetic equations for the process are obtained and shown in Table 6.

At different temperatures, all of the values of a and b are very small compared to the values of k_2 and k. This indicates that the Burton–Cabrera–Frank dislocation theory can be used successfully for describing the dilution/crystallization process of FOX-7 in DMSO –H_2O system.

Eq. (13) [12] was applied to calculate the values of activation energy E and pre-exponential factor A by the slope and the intercept of the linear in Fig. 1. The correlative coefficient of the line is 0.985.

$$\ln\ k = \ln A - \frac{E}{RT} \tag{13}$$

Table 6
The kinetics of dilution/crystallization process for FOX-7 in DMSO-H_2O system.

T (K)	H_∞ (J g^{-1})	$\mathrm{d}H/\mathrm{d}t = H_\infty k(1-(H/H_\infty))^n$			$\mathrm{d}H/\mathrm{d}t = k_2(1-(H/H_\infty)+a)$			$\mathrm{d}m/\mathrm{d}t = km_\infty(c-c_\infty)+b$	
		$k \times 10^3$ (s^{-1})	n	r	$k_2 \times 10^3$ (J s^{-1})	$a \times 10^3$ (J s^{-1})	r	$k \times 10^5$	$b \times 10^7$
301.15	124.4	0.61	0.7543	0.9991	0.03	0.013	0.9970	4.91	1.05
308.15	209.9	1.01	0.7587	0.9961	0.19	0.033	0.9963	5.92	1.57
313.15	235.1	1.24	0.7454	0.9991	0.27	0.046	0.9967	13.6	1.96
318.15	464.8	1.89	0.7222	0.9982	0.94	0.21	0.9977	18.5	4.52

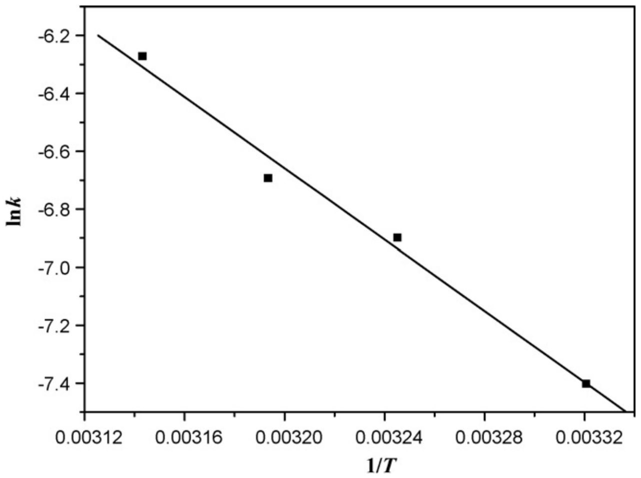

Fig. 1. The relationship of reaction rate constant (k) vs. temperature (T) for FOX-7 in DMSO–H_2O system.

The values of E of $5.098 \times 10^4\,\mathrm{J\,mol^{-1}}$ and A of $4.27 \times 10^5\,\mathrm{s^{-1}}$ indicate that the reaction can take place easily at 301.15–318.15 K.

4. Conclusions

(1) The expressions describing values of $\Delta_{\mathrm{diss}}H$, $\Delta_{\mathrm{diss}}H_{\mathrm{apparent}}$ and $\Delta_{\mathrm{diss}}H_{\mathrm{partial}}$ vs. the concentration of FOX-7 in DMSO are $\Delta_{\mathrm{diss}}H = 8.2146 - 207.343b^{1/2} + 629.7194b$, $\Delta_{\mathrm{diss}}H_{\mathrm{apparent}} = -207.343b^{1/2} + 629.7194b$ and $\Delta_{\mathrm{diss}}H_{\mathrm{partial}} = 1259.44b - 311.0145b^{1/2}$, respectively.

(2) The kinetic equation of dissolution in DMSO of FOX-7 at 298.15 K is $\mathrm{d}\alpha/\mathrm{d}t = 1.12 \times 10^{-8}(1-\alpha)^{0.7}$.

(3) The dilution/crystallization growth process of FOX-7 in DMSO–water system accords with the Burton–Cabrera–Frank dislocation theory. The value of E of this process is very small, indicating that the reaction easily takes place.

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