Investigation of the Dilution/Crystallization Dynamics of RDX and HMX by Microcalorimetry

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Abstract: Three thermokinetic equations describing the crystal growth process and two relationships between the parameters and the constants of the kinetic equations are derived The total heat produced and the rate of heat production during the dilution/crystallization of RDX and HMX from dimethyl sulfoxide, cyclohexanone and nitric acid are measured using a Calvet microcalorimeter and a model RD-1 conduction calorimeter The thermokinetic data of crystal growth processes of RDX and HMX are treated based on the derived equations and relationships The results show that the exothermic dilution/crystallization processes of RDX and HMX accord with the Burton-Cabrera-Frank dislocation theory.

Key words: single compound explosive; crystallization dynamics; RDX; HMX; dislocation theory

RDX   HMX   /

1,3,   1,   1,   1,   2,   3,   3

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:   3   2   Calvet

RDX   HMX   /

RDX   HMX   /   , RDX   HMX   /

Burton-Cabrera-Frank

:   ;   ; RDX; HMX;

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Introduction

RDX and HMX are two widely used nitramine explosives and energetic ingredients of propellants In two previous notes[1,2], the crystallization kinetics of RDX and HMX from DMSO and cyclohexanone, and that of HMX from HNO$_3$ were reported The aim of this work is to explore the adaptability of the thermokinetic equations to the crystal growth processes of RDX and HMX and obtaining the information about the interdependence between the parameters and the constants of different kinetic equations

1 Derivation of the kinetic equations of the crystal growth process

In order to analyze the kinetics of the crystal growth process of RDX and HMX, the following general form of the crystal growth process is used

$$
\begin{array}{lllll}
A (aq) & — & A (s) & + & heat \\
t = 0, & C_0 & 0, 0 & & 0 \\
t = t, & C & m, \alpha & & H \\
t = , & C & m , \alpha = 1 & & H
\end{array} \quad (1)
$$

where, assuming that in forming the crystal A (s) from A (aq), C is the solute concentration in the solution at time t (g/100 g solvent). C is equilibrium staturation concentration (g/100 g solvent). m and α are the mass and fraction of solid deposited during a certain time, respectively. H is the heat produced during a certain time t, and when $t = 0$, $C = C_0$, $m = 0$, $\alpha = 0$ and $H = 0$, when $t = $, $C = C$, $m = m$, $\alpha = \alpha = 1$ and $H = H$.

The relationship between the energy change (i. e. the heat produced) of a reacting system and the extent (i. e. mass or fraction or concentration) of the reaction (1) may be expressed as

$$\frac{C_0 - C}{C_0 - C} = \frac{0 - m}{0 - m} = \frac{0 - \alpha}{0 - \alpha} = \frac{0 - H}{0 - H} \quad (2)$$

From eq. (2), we obtain

$$\alpha = \frac{H}{H} \quad (3)$$

$$\frac{d\alpha}{dt} = \frac{1}{H} \frac{dH}{dt} \quad (4)$$

$$\frac{dm}{dt} = \left[\frac{m}{H}\right] \frac{dH}{dt} \quad (5)$$

and

$$\frac{C - C}{C_0 - C} = \left[1 - \frac{H}{H}\right] \quad (6)$$

Inserting eqs. (3) and (4) into the differential kinetic equation (7) of the reaction of the nth order

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

The thermokinetic equations (8) and (9) are obtained:

$$\frac{dH}{dt} = H\ k\left[1 - \frac{H}{H}\right]^n \quad (8)$$

and

$$\ln\left[\frac{1}{H}\left[\frac{dH}{dt}\right)_i\right] = \ln k + n \ln\left[1 - \left(\frac{H}{H}\right)_i\right]$$
$$i = 1, 2 \ldots L \quad (9)$$

where H is the total heat produced (corresponding to the global area under the thermokinetic curve); H_i is the heat produced in a certain time (corresponding to the partial area under the curve); dH_i/dt is the rate of heat production at time t; k and n are the rate constant and reaction order of the crystal growth, respectively.

When $\ln\left[\frac{1}{H}\left[\frac{dH}{dt}\right)_i\right]$ is plotted versus ln

$\left[1 - \left(\frac{H}{H}\right)_i\right]$ by the least-squares method, this gives the value of n from the slope and k from the intercept.

Equation (8) is known as the general form describing the crystal growth process.

According to the Burton-Cabrera-Frank (BCF) dislocation theory[3], for relatively high supersaturation, the rate of crystal growth at time t, dm/dt may be expressed as

$$\frac{dm}{dt} = km\ (C - C) \quad (10)$$

The combination of eqs. (5), (6) and (10) gives

$$\frac{dH}{dt} = kH\ (C_0 - C)\left[1 - \frac{H}{H}\right] = k_1\left[1 - \frac{H}{H}\right] \quad (11)$$

where

$$k_1 = kH\ (C_0 - C) \quad (12)$$

If $C_0 >> C$, we have

$$\frac{dH}{dt} = kH\ C_0\left[1 - \frac{H}{H}\right] = k_2\left[1 - \frac{H}{H}\right] \quad (13)$$

where

$$k_2 = kH\ C_0 \quad (14)$$

when $\left(\frac{dH}{dt}\right)_i$ is plotted versus $1 - \left(\frac{H}{H}\right)_i$ by the least-squares method, this gives the values of k_2 and a in the equation (15)

$$\frac{dH}{dt} = k_2\left[1 - \frac{H}{H}\right] + a \quad (15)$$

If equation (10) is written as

$$\frac{dm}{dt} = km\ (C - C) + b \quad (16)$$

The equation (17) is obtained by combining eqs. (5), (6) and (16)

$$\frac{dH}{dt} = \frac{dm}{dt}\left(\frac{H}{m}\right) = \frac{H}{m}[km\ (C - C) + b]$$
$$= \frac{H}{m}\left[km\ (C_0 - C)\left(1 - \frac{H}{H}\right) + b\right]$$
$$= H\ k(C_0 - C)\left(1 - \frac{H}{H}\right) + \frac{bH}{m}$$
$$= H\ kC_0\left(1 - \frac{H}{H}\right) + \frac{bH}{m}\ (C_0 >> C)$$
$$(17)$$

Comparing eq. (15) with eq. (17), two relationships [eqs. (18) and (19)] are obtained

$$k = k_2/H\ C_0 \quad (18)$$

and

$$b = \alpha n \ /H \tag{19}$$

Equations (18) and (19) relate k to k_2 and b to a, respectively.

If the values of the constants a and b are small in comparison with those of k_2 and k, the kinetics of the crystal growth processes can be expressed by eqs (10) and (13).

Equations (10) and (13) are known as the thermokinetic equations of the crystal growth process. Equation (13) is only an especial example ($n = 1$) of equation (8).

2 Experimental

2.1 Materials

RDX and HMX used as solutes were prepared by our institute. The RDX contained no detectable HMX, and HMX contained no detectable RDX. Their purities were more than 99.9%. DMSO (m. p. 16.5～19 ; $r_4^{20} = 1.098～1.106$) and cyclohexanone (b. p. 154.0～156.0 ; $n_D^{20} = 1.4500～1.4510$) used as solvents are of chemical and analytical purity respectively. The concentration of HNO_3 used as solvent was 95.68%. A 50.10% DMSO-H_2O mixture and n-C_7H_{16}/CCl_4 (1:1, V/V) are used as diluents, where H_2O is twice distilled water; n-C_7H_{16} (b. p. 96.5～98.5 ; $r_4^{20} = 0.683～0.686$) and CCl_4 (b. p. 75.5～77.5 ; $r_4^{20} = 1.591～1.597$) are of chemical purity.

2.2 Experimental equipment and conditions

All measurements at 30 are made using a Calvet microcalorimeter, type BT-215 from SETARAM, France, which has a sensitivity of 66.5 $\mu V \cdot mW^{-1}$ and is equipped with two 15 ml vessels. All measurements at 34 are made using a conduction calorimeter, type RD-1 from Sichuan University, with a precision of ± 0.5% and equipped with two 60 ml vessels. The microcalorimeter is calibrated by the Joule effect and the calibration is repeated after each experiment.

The precision of enthalpy measurement is 2%. The device used for the study of the crystallization kinetics is shown in Fig. 1. (1. thin glass bulb containing diluent; 2. polytetrafluoroethylene tube; 3. glass tube containing RDX or HMX solution; 4. silicon rubber cover; 5. calorimetric cell; 6. glass rod. On depressing the rod, the bottom of the glass bulb is broken, and the solution and diluent mix together in the tube).
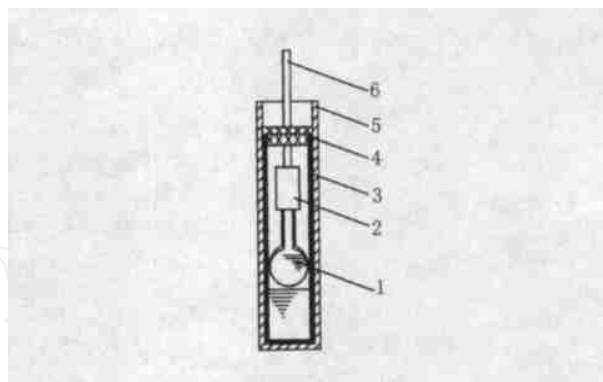
Fig 1 Device used for measuring the crystallization-kinetics

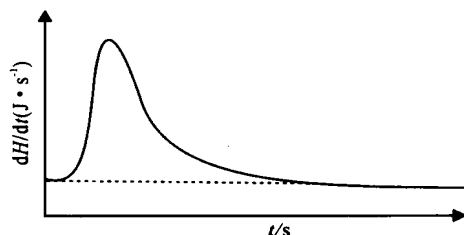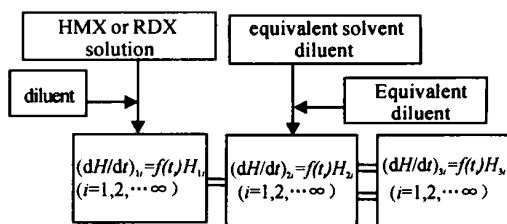Fig 2 Typical thermogram obtained during dilution/crystallization

Fig 3 Block diagram of the process of studying dilution/crystallization kinetics

A typical schematic thermogram obtained during the dilution and crystallization is shown in Fig. 2, and is obtained by the testing and computing method presented as a block diagram in Fig. 3.

In Fig. 3, $(dH/dt)_{1i}$ is the rate of total heat

production at time t, including the rate of the heat of mixing produced between solvent and diluent, $(dH/dt)_{2i}$, and the rate of the heat of crystallization of the crystal, $(dH/dt)_{3i}$ at time t; and H_{1i} is the total heat produced during a certain time, including the heat of mixing produced between solvent and diluent, H_{2i}, and the heat of crystallization by the crystal during a certain time.

The thermograms obtained under the same conditions overlapped with each other, indicating that the reproducibility of tests was satisfactory.

3　Results and discussion

To verify the reliability of eqs (8), (15) and (16) and obtain information about the kinetic parameters and the constants of RDX and HM X, the original thermokinetic data tabulated in Table 1 are fitted to the eqs (8), (15) and (16) by the linear least-squares method. Results obtained, including the total heat produced, the reaction order (n), the rate constants (k_2 and k) during the crystallization of RDX and HM X from DM SO and cyclohexanone at 30 and that of HM X from HNO$_3$ at 34, and the constants (a and b) in eqs (15) and

(16), are shown in Table 2

From Tables 1 and 2, the following observations can be made:

(1) The crystal growth processes of RDX and HM X are exothermic. The exothermic process may be expressed by the isothermal differential kinetic equation (8)

(2) BCF model [eq. (13)] is only an especial example ($n = 1$) of the general form [eq. (8)] of the crystal growth process

(3) Because $k_2 >> d$ in [eq. (15)] and $k >> b$ in [eq. (16)], describing the kinetics of the crystal growth processes of RDX and HM X by the eqs (15) and (16) are tenable. This indicates that the crystal growth processes of RDX and HM X from DM SO and cyclohexanone and that of HM X from HNO$_3$ without seeds of HM X accords with the BCF dislocation theory.

(4) In our experimental conditions, the crystal growth process of HM X from HNO$_3$ with seeds of HM X is out of accord with the BCF dislocation theory.

Table 1　Thermokinetic data of the crystal growth processes of RDX and HM X

Experimental conditions No. 1				Experimental conditions No. 2				
Tempe. 30	Solute	Solvent	Seed	Diluent	Tempe. 30	Solute	Solvent	Seed	Diluent
	RDX (0.0084g)	DM SO (0.0250g)		50.1% DM SO-H$_2$O (0.6896g)		RDX (0.0084g)	DM SO (0.0250g)	RDX (0.4000g)	50.1% DM SO-H$_2$O (0.6896g)
t/s	$(dH/dt)_i/10^4$ (J·s^{-1})		$(H_t)_i/10^2$J		t/s	$(dH/dt)_i/10^4$ (J·s^{-1})			$(H_t)_i/10^2$J
210	6.991		2.761		210	10.00			15.69
240	6.255		5.146		240	8.841			18.58
270	6.092		7.155		270	8.251			21.13
300	5.573		9.372		300	7.372			23.47
330	5.196		11.00		330	6.640			25.61
360	4.749		12.84		360	6.050			27.61
390	4.297		14.69		390	5.460			29.54
420	4.134		16.15		420	5.012			30.96
450	3.686		17.61		450	4.711			32.76
480	3.655		19.08		480	4.263			34.18
510	3.502		20.17		510	4.100			35.19
540	3.197		21.25		540	3.937			36.40
570	3.033		22.38		570	3.494			37.61
600	2.870		23.47		600	3.188			38.66

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Table 1　Thermokinetic data of the crystal growth processes of RDX and HMX

Experimental conditions No. 1

Tempe. 30	Solute RDX (0.0084g)	Solvent DMSO (0.0250g)	Seed 50.1%	Diluent DMSO-H₂O (0.6896g)
t/s		$(dH/dt)_i/10^4 (J \cdot s^{-1})$		$(H_t)_i/10^2 J$
630		2.506		24.31
660		2.544		25.48
690		2.523		26.40
720		2.218		27.15
750		2.054		28.07
780		1.891		28.79
810		1.728		29.33
840		1.565		30.25
		0		42.72

Experimental conditions No. 2

Tempe. 30	Solute RDX (0.0084g)	Solvent DMSO (0.0250g)	Seed RDX 50 (0.4000g)	Diluent 1% DMSO-H₂O (0.6896g)
t/s		$(dH/dt)_i/10^4 (J \cdot s^{-1})$		$(H_t)_i/10^2 J$
630		3.025		39.66
660		2.720		40.67
690		2.845		41.51
720		2.540		42.17
750		2.234		42.97
780		2.075		43.81
810		2.054		44.21
840		1.895		44.65
		0		44.73

Experimental conditions No. 3

Tempe. 30	Solute HMX (0.0022g)	Solvent cyclohexanon (0.1000g)	Seed HMX (0.4771g)	Diluent n-C₇H₁₆/CCl₄ (1:1) (0.9555g)
t/s		$(dH/dt)_i/10^5 (J \cdot s^{-1})$		$(H_t)_i/10^2 J$
210		118.2		22.18
240		98.24		26.57
270		88.20		30.59
300		80.75		34.06
330		68.16		36.78
360		58.12		39.16
390		46.69		41.34
420		40.96		43.18
450		35.19		44.60
480		26.61		44.73
510		22.30		46.78
540		17.99		47.66
570		12.26		48.37
600		7.949		48.91
630		3.598		49.21
		0		49.33

Experimental conditions No. 4

Tempe. 34	Solute HMX (0.3648g)	Solvent HNO₃ (2.8685g)	Seed	Diluent H₂O (0.7910g)
t/min		$(dH/dt)_i/(J \cdot min^{-1})$		$(H_t)_i/J$
1.25		19.54		6.109
1.50		19.63		10.79
2.00		19.87		19.25
2.25		21.34		25.44
2.50		15.77		29.62
2.75		13.81		33.30
3.00		13.43		37.28
5.50		6.987		62.59
6.50		5.565		68.53
7.50		4.770		74.27
8.50		3.138		78.58
10.5		2.887		83.89
12.5		2.092		87.70
13.5		1.674		89.62
14.5		1.297		90.88
		0		93.64

Experimental conditions No. 5

Tempe. 34	Solute HMX (0.3684g)	Solvent HNO₃ (2.8685g)	Seed HMX (0.2089g)	Diluent H₂O (0.7910g)
t/min		$(dH/dt)_i/(J \cdot min^{-1})$		$(H_t)_i/J$
1.00		42.63		30.54
1.25		24.02		38.45
1.50		14.39		43.39
1.75		13.22		46.40
2.00		9.623		49.54
2.75		8.326		56.44

Experimental conditions No. 5

Tempe. 34	Solute HMX (0.3684g)	Solvent HNO₃ (2.8685g)	Seed HMX (0.2089g)	Diluent H₂O (0.7910g)
t/min		$(dH/dt)_i/(J \cdot min^{-1})$		$(H_t)_i/J$
5.50		5.397		77.65
7.50		3.556		83.81
9.50		2.176		88.70
12.5		1.297		94.14
		0		102.4

Table 2   Total heat produced and crystal growth kinetics of RDX and HM X

T /	H / (J· g⁻¹)	$\dfrac{\mathrm{d}H}{\mathrm{d}t}=H\ k\left[1-\dfrac{H}{H}\right]^{n}$			$\dfrac{\mathrm{d}H}{\mathrm{d}t}=k_2\left[1-\dfrac{H}{H}\right]+a$			$\dfrac{\mathrm{d}H}{\mathrm{d}t}=km\ (C-C)+b$	
		$k\times 10^3/\mathrm{s}^{-1}$	n	r	$k_2\times 10^4/(\mathrm{J}\cdot\mathrm{s}^{-1})$	$a\times 10^5/(\mathrm{J}\cdot\mathrm{s}^{-1})$	r	$k\times 10^3/\mathrm{s}^{-1}$	$b\times 10^6/(\mathrm{g}\cdot\mathrm{s}^{-1})$
30	50. 86	1. 74	1. 22	0. 997	8. 09	- 8. 01	0. 997	1. 60	- 1. 57
30	53. 25	1. 68	0. 307	0. 984	12. 0	16. 8	0. 996	4. 47	3. 15
30	224. 2	3. 23	0. 640	0. 996	20. 3	11. 0	0. 991	19. 7	0. 049
34	256. 7	3. 68	0. 844	0. 986	3810	400	0. 981	0. 408	15. 6
34	268. 1	5. 75	1. 38	0. 958	7710	- 10500	0. 822	0. 775	- 392

(5) With the addition of seed crystals of RDX and HM X, the value of k in eq. (16) is larger than that of k without seeds. This shows that the total number of nuclei in the seeded solution is greater than that in unseeded solution.

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