Thermochimica Acta, 173 (1990) 193–198
Elsevier Science Publishers B.V., Amsterdam

INVESTIGATION OF THE CRYSTALLIZATION KINETICS OF CYCLOTRIMETHYLENETRINITRAMINE AND CYCLOTETRAMETHYLENETETRANITRAMINE BY MICROCALORIMETRY

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(Received 25 April 1990)

ABSTRACT

The total heat produced and the rate of heat production during the crystallization of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) from dimethyl sulfoxide and cyclohexanone are measured using a Calvet microcalorimeter. The data of their thermograms are treated based on the dislocation theory model. The results show that the crystal growth processes of RDX and HMX accord with the dislocation theory.

INTRODUCTION

Cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are two widely used nitramine explosives and energetic ingredients of propellants. The crystallization kinetics of HMX have never been reported so far. The crystallization kinetics of RDX have been studied only in one paper [1]. Before this study, microcalorimetry has not been used to investigate such kinetics. The aim of this work is to study the crystallization kinetics of RDX and HMX from dimethyl sulfoxide (DMSO) and cyclohexanone. This is quite useful in studying their industrial crystallization processes.

DERIVATION OF THE KINETIC EQUATION 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

$$\begin{array}{lll}
\mathrm{A(aq)} \rightarrow & \mathrm{A(s)} & + \text{ heat} \\
t = 0,\ C_0 & 0 & 0 \\
t = t,\ C & m & Q \\
t = \infty,\ C_\infty & m_\infty & Q_\infty
\end{array}$$

where C is the solute concentration in the solution at time t; m is the mass of solid deposited during a certain time t; Q is the heat produced during a certain time t. When $t = 0$, $C = C_0$, $m = 0$ and $Q = 0$; when $t = \infty$, $C = C_\infty$, $m = m_\infty$, and $Q = Q_\infty$.

The relationship [2] between the energy change (i.e. the heat produced) of a reacting system and the extent (i.e. mass or concentration) of the reaction is given by

$$\frac{Q}{Q_\infty} = \frac{m}{m_\infty} = \frac{C_0 - C}{C_0 - C_\infty} \tag{1}$$

From eqn. (1), we have

$$\frac{dm}{dt} = \left(\frac{m_\infty}{Q_\infty}\right)\frac{dQ}{dt} \tag{2}$$

and

$$\frac{C - C_\infty}{C_0 - C_\infty} = \left(1 - \frac{Q}{Q_\infty}\right) \tag{3}$$

According to the Burton–Cabrera–Frank (BCF) dislocation theory [3], for relatively high supersaturations, the rate of crystal growth (dm/dt) is as follows

$$\frac{dm}{dt} = km_\infty(C - C_\infty) \tag{4}$$

where k is the rate constant of crystal growth.

The combination of eqns. (2), (3) and (4) gives

$$\frac{dQ}{dt} = k_1\left(1 - \frac{Q}{Q_\infty}\right) \tag{5}$$

where $k_1 = kQ_\infty(C_0 - C_\infty)$.
If $C_0 \gg C_\infty$, we have

$$\frac{dQ}{dt} = k_2\left(1 - \frac{Q}{Q_\infty}\right) \tag{6}$$

where $k_2 = kQ_\infty C_0$.

Equations (4) and (6) are known as the kinetic equations of the crystal growth process.

EXPERIMENTAL

Materials

RDX and HMX used as solutes were prepared by our Institute. The RDX contained no detectable HMX, and HMX contained no detectable RDX.

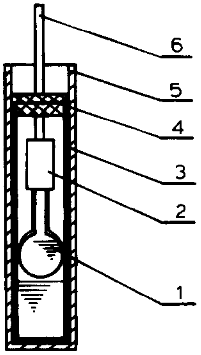

Fig. 1. Device used for measuring the crystallization kinetics of RDX and HMX. 1, Thin glass bulb containing diluent; 2, polytetrafluoroethylene tube; 3, glass tube containing RDX or HMX solution; 4, silicon rubber cover; 5, calorimetric cell; 6, glass rod. On depressing the rod, the bottom of the glass bulb is broken, and the solution and diluent mix together in the tube.

Their purities were more than 99.9%. DMSO (m.p. 16.5–19 °C; $r_4^{20} = 1.098$–1.106) and cyclohexanone (b.p. 154.0–156.0 °C; $n_D^{20} = 1.4500$–1.4510) used as solvents are of chemical and analytical purity respectively. 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 °C; $r_4^{20} =$ 0.683–0.686) and CCl_4 (b.p. 75.5–77.5 °C; $r_4^{20} = 1.591$–1.597) are of chemical purity.

Experimental equipment and conditions

All measurements are made using a Calvet microcalorimeter, type BT 215 from SETARAM, France, which has a sensitivity of 66.5 $\mu V\ mW^{-1}$ and is equipped with two 15-ml vessels. The microcalorimeter is calibrated by the Joule effect and the calibration is repeated after each experiment. The

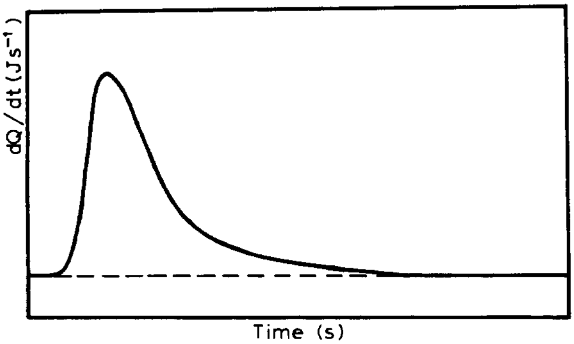

Fig. 2. Typical thermogram obtained during dilution/crystallization.

TABLE 1

Total heat produced and crystal growth kinetics of RDX and HMX

Temp. (°C)	Solute (amount in g)	Solvent (amount in g)	Seed (amount in g)	Diluent (amount in g)	Q_∞ (J g^{-1})	$\frac{dQ}{dt} = k_2\left(1 - \frac{Q}{Q_\infty}\right) + a$			$\frac{dm}{dt} = km_\infty(C - C_\infty) + b$	
						$k_2 \times 10^4$	$a \times 10^5$	r	$k \times 10^3$	$b \times 10^5$
30	RDX (0.0084)	DMSO (0.0250)		50.10% DMSO–H_2O (0.6896)	52.6	9.41	12.7	0.99	1.80	2.41
					53.7	8.12	15.3	0.97	1.52	2.84
					52.2	7.20	4.64	0.99	1.39	0.89
					50.9	8.05	−7.78	0.99	1.59	−1.53
				Mean	52.3	8.20	6.22		1.58	1.55
30	RDX (0.0084)	DMSO (0.0250)	RDX (0.4000)	50.10% DMSO–H_2O (0.6896)	52.8	13.6	−27.0	0.99	2.60	−0.51
					53.2	12.0	16.9	0.99	2.28	3.17
				Mean	53.0	12.8	−5.05		2.44	2.66
30	HMX (0.0022)	cyclohexanone (0.1000)	HMX (0.4771)	n-C_7H_{16}/CCl_4 (1:1) (0.9655)	224	20.1	11.6	0.99	20.4	0.52
					227	20.0	2.0	0.99	20.0	0.09
				Mean	225	20.1	6.8		20.2	0.31

Q_∞, total heat produced (J g^{-1}); dQ/dt, rate of heat production at time t (J s^{-1}); k_2 rate constant of crystal growth (J s^{-1}); Q, heat production at time t (J); a, constant; dm/dt, rate of crystal growth at time t (g s^{-1}); k, rate constant of crystal growth (s^{-1}); m_∞, total mass of solid deposited (g); C, solute concentration in the solution (g/100 g solvent); C_∞, equilibrium saturation concentration (g/100 g solvent); b, constant.

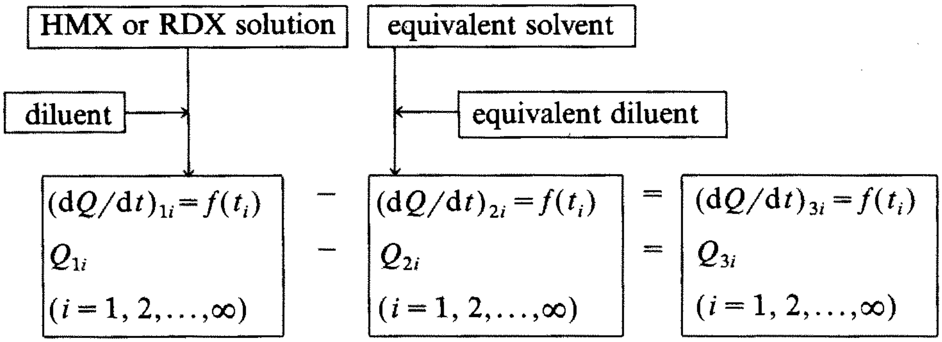

Fig. 3. Block diagram of the process of studying dilution/crystallization kinetics.

precision of enthalpy measurement is 2%. Measurements of the crystallization kinetics of RDX and HMX are carried out at 30 °C. The device used for the study of the crystallization kinetics is shown in Fig. 1.

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

RESULTS AND DISCUSSION

The total heat produced (Q_∞) and the rate constants during the crystallization of RDX and HMX from DMSO and cyclohexanone at 30 °C are listed in Table 1.

From Table 1 the following observations can be made.

With the addition of seed crystals of RDX, the value of k_2 (or k) is larger than that of k_2 (or k) without seeds. This shows that the total number of nuclei in the seeded solution is greater than that in the unseeded solution.

Because 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 of RDX and HMX can be expressed by eqns. (4) and (6). This fact indicates that the crystal growth processes of RDX and HMX from DMSO and cyclohexanone accord with the BCF dislocation theory model.

CONCLUSIONS

It is possible to study the crystallization kinetics by measuring the heat produced and the rate of heat production using a Calvet microcalorimeter.

The crystallization kinetics of RDX and HMX from DMSO and cyclohexanone can be expressed by the BCF dislocation theory model.

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