

CRYSTALLIZATION OF HMX FROM γ -BUTYROLACTONE*

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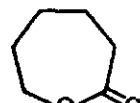
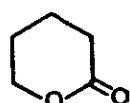
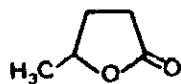
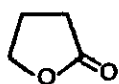
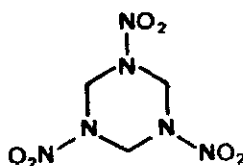
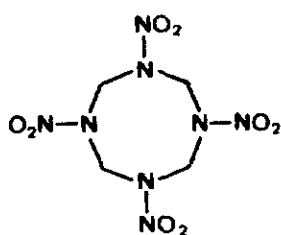
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Summary

A method for recrystallization of HMX from γ -butyrolactone has been developed. The method produces well-shaped crystals of the desired β -modification. The crystallization can be performed either as a cooling crystallization or as a watering-out precipitation. Depending on the cooling programme used, the particle size distribution can be varied.

Introduction

There are three main reasons for recrystallizing a crystalline compound. Firstly, it is a way of purifying the product, the undesirable byproducts remaining in the solvent after crystallization. Secondly, crystallization can result in a specific modification and crystal habit, these being dependent upon the solvent and the crystallization conditions. Thirdly, in many cases it is desirable to obtain a specific particle size distribution and this is very much dependent upon the process conditions. All of these aspects are very important in the crystallization of HMX (1) and RDX (2).



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TABLE 1

Solubility of HMX in some lactones

Solvent	Solubility (g) of HMX in 100 g solvent	
	23°C	120°C
γ -butyrolactone (3)	11.0	48.1
γ -valerolactone (4)	9.2	35.5
δ -valerolactone (5)	6.5	35.7
ϵ -caprolactone (6)	6.8	38.3

HMX occurs in four different crystal modifications, two of which, α and β , can be readily obtained. Of these two, β is preferred since it has the highest density and the lowest sensitivity. The crystal modification which is obtained is largely determined by the choice of solvent used for the recrystallization.

Solvents which have previously been used for crystallization of HMX are acetone and cyclohexanone, both of which are known to give β -HMX. However both solvents have a rather low solubility for HMX. Amongst the solvents with higher solvent capacities which have been tested is dimethylsulfoxide [1].

In the present work we have examined the use of different lactones (3–6) for recrystallizing both HMX and RDX (Table 1). Some of these, e.g. γ -butyrolactone and δ -valerolactone, have been tested before and were then shown to give complexes with HMX [2, 3]. However, we have found that HMX can be recrystallized in a simple manner to give β -HMX of good purity and shape. γ -Butyrolactone was found to be the best of the lactones tested, considering both solvent capacity and cost.

Crystallization

γ -Butyrolactone has many properties which makes it an excellent solvent for recrystallization of HMX (Table 2). It has a relatively low toxicity, a boiling

TABLE 2

Physical and toxicological data for γ -butyrolactone

Boiling point	206°C
Melting point	-42°C
Miscibility with water	∞
Density	1.13 g/cm ³
Vapour pressure (RT)	0.1 kPa (1 mmHg)
Flame point	92°C
LD_{50} (oral dose, rat)	800–1600 mg/kg
LD_{50} (skin, guinea pig)	~5600 mg/kg

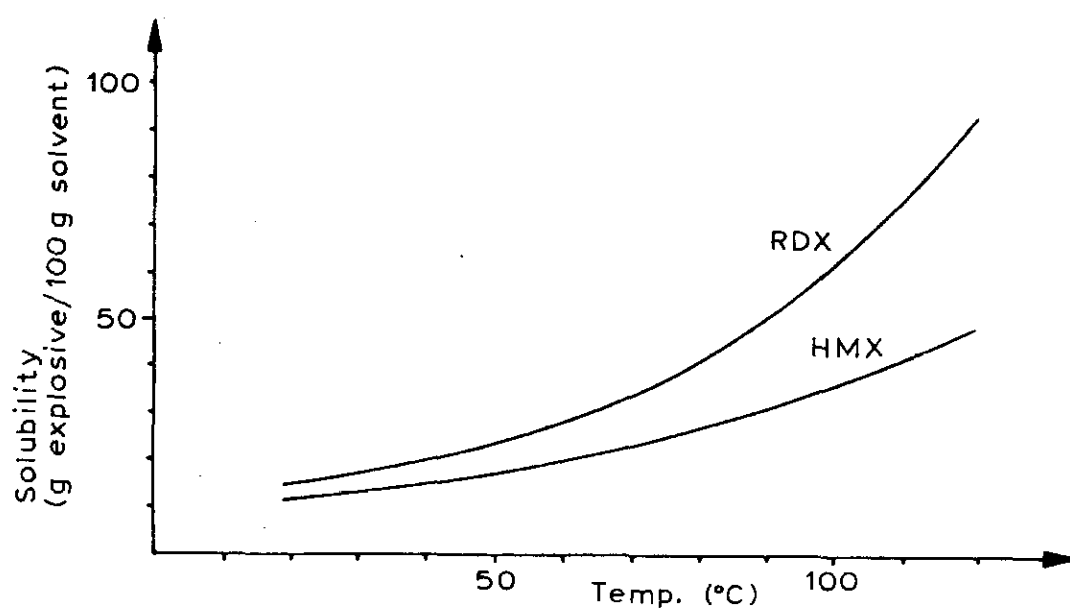


Fig. 1. Solubility curves of HMX and RDX in γ -butyrolactone.

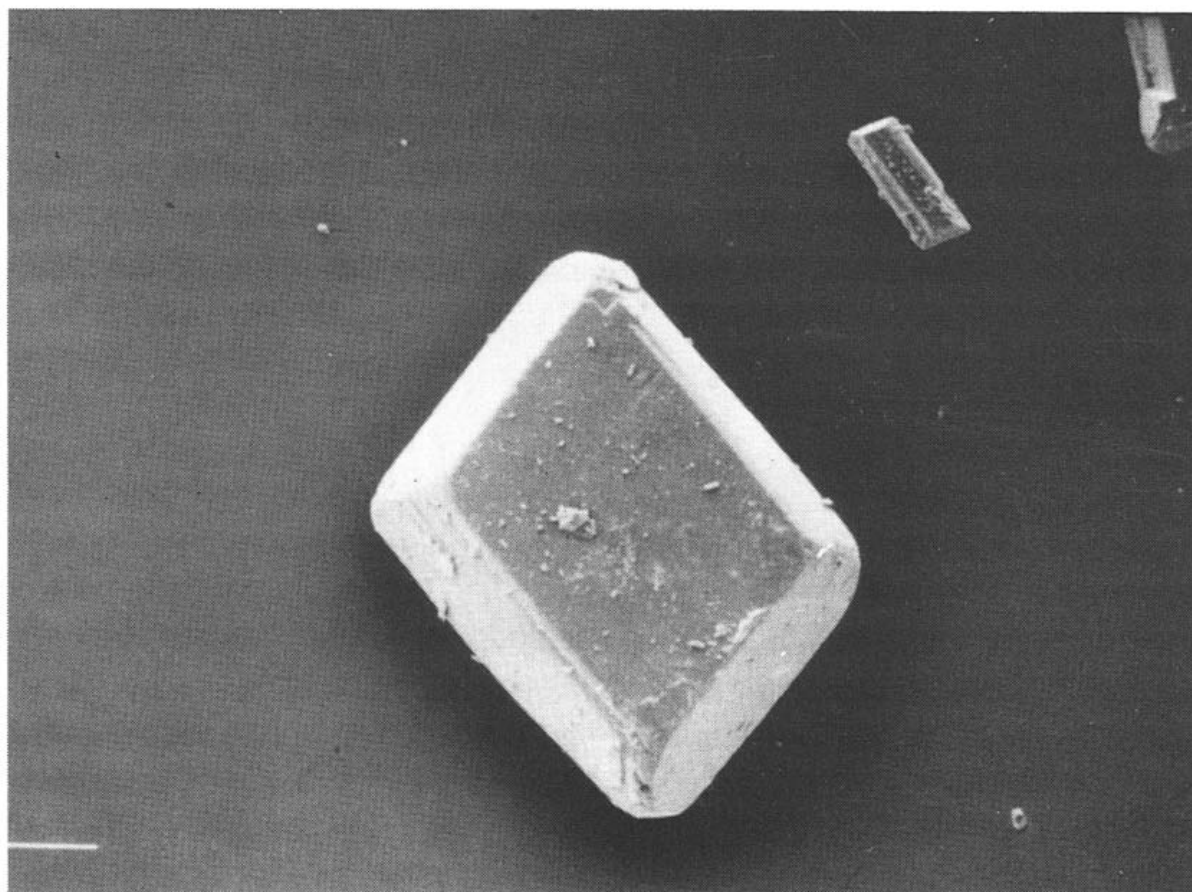


Fig. 2. Scanning electron micrograph of β -HMX ($\times 50$).

point of 206°C and a density of 1.13 g/cm^3 , and has a solvent capacity for HMX and RDX which is strongly temperature dependent (Fig. 1). HMX can be crystallized from γ -butyrolactone in the desired β -modification without any detectable amount of α -HMX. The crystals are well shaped and have a relatively low tendency to form crossed crystals or other irregularities (Fig. 2).

Crude HMX contains some water and acetic acid and, after suspending the HMX in the lactone, these should at least partially be distilled off before the

crystallization is started, otherwise the solvent capacity of the lactone will be diminished too much. The solubility of HMX in γ -butyrolactone containing 6% acetic acid and 1% water is 10.4 g/100 g solvent at 23°C and 39.1 g/100 g solvent at 120°C. Nevertheless, the solvent may be reused many times before it has to be redistilled.

The crystallization can be performed either as a cooling crystallization or as a precipitation. Using different cooling programmes, the particle size distribution can be easily controlled. With natural cooling (Fig. 3) in a 500 l crystallizer with a cooling mantle and cooling coils, it is advisable to saturate the solution at 120°C. The resulting median particle diameter (MPD) was found to be consistently around 150 μm (Fig. 4, curve 1). With a more effi-

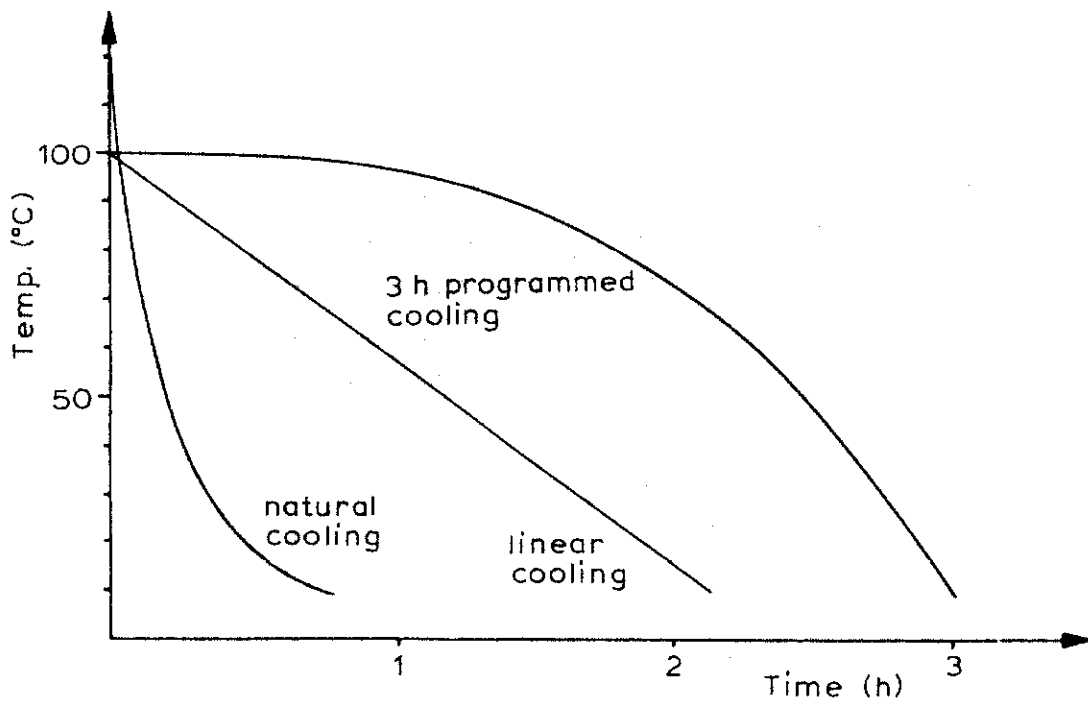


Fig. 3. Cooling curves.

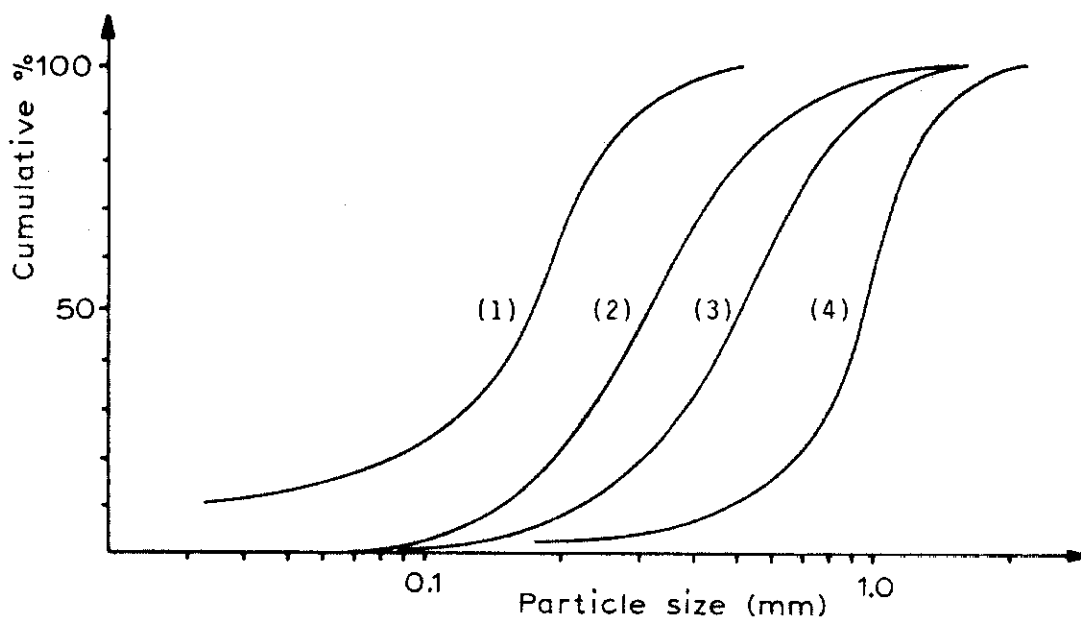


Fig. 4. Crystal size distribution. Curve 1: natural cooling; curve 2: 3 h cooling programme; curve 3: 6 h cooling programme; curve 4: 6 h programme with seeding.

cient cooling system it is possible to obtain median particle diameters of 60–70 μm .

To obtain coarser particles programmed cooling must be used. This produces a lower nucleation rate combined with a high crystal growth rate. The cooling sequence we have used is defined according to the formula

$$\frac{T_0 - T}{T_0 - T_f} = \frac{t^3}{t_t^3}$$

where T_0 is the starting temperature, T_f the final temperature, t_t the total cooling time and T the temperature at time t .

When long crystallization times are used, it is desirable to avoid high temperatures, since the decomposition of HMX is otherwise significant. To obtain crystals with MPD of 500 μm using a cooling period of 6 h, we began the cooling programme at 100°C using 35 g HMX/100 g γ -butyrolactone (Fig. 4, curve 3). When cooling programmes intermediate between fast cooling and a 6 h programme according to the formula above are employed, the particle size distribution can be varied in different ways. For example a linear cooling of 0.7°C/min gave a rather broad size distribution around 500 μm , while a 3 h programme (Fig. 4, curve 2) gave a median particle diameter of 320 μm . To obtain even coarser crystals it is necessary to seed the solution. The best result was obtained using rather coarse seeds (around 500 μm). This produced crystals with MPD of 900 μm (Fig. 4, curve 4). The seeds are added to the crystallizer just after the solubility curve has been crossed. If the seeds are added too soon they dissolve, while addition near the supersaturation limit causes spontaneous nucleation.

Natural cooling gives class A in the military specification MIL-H-45444B, a 3 h cooling programme gives class C, and a 6 h cooling programme with seeding gives class D. The outcome of a crystallization is very much dependent upon the crystallizer used. Therefore a new set of parameters must be experimentally determined, with the aid of theoretical considerations, when changing from one crystallizer to another.

To obtain very fine particles it is useful to precipitate HMX from an HMX/ γ -butyrolactone solution using water; at least an equal volume of water should be used. The mixing can be done either in a static mixer or directly in the crystallization vessel. The crystals obtained usually have MPD values between 5 and 35 μm , depending upon the exact conditions used.

The above mentioned methods can also be used to recrystallize RDX and produce well-shaped crystals of spherical form.

Complex formation

When crystallizing crude HMX containing water and acetic acid from γ -butyrolactone, complex formation with the solvent can occur under certain conditions. We determined whether or not complex formation had occurred by differential scanning calorimetry and by gas chromato-

graphy. The DSC curve of pure β -HMX exhibits an endotherm around 193°C, while the HMX/ γ -butyrolactone complex has an endotherm at 87°C. The ratio of solvent to HMX (mol/mol) in the crystallized sample before washing with water was between 0.54 and 0.85 when the complex was formed, and between 0.01 and 0.03 when it was not. After washing with water the solvent content was lower than 0.01%. In the presence of low concentrations of water and acetic acid the complex is usually at least partially formed. For example we could detect complex formation in the presence of 5% water, and 3% water plus 3% acetic acid. With 4% water plus 4% acid no complex could be detected. In a normal crystallization it is therefore possible that the complex is initially formed, but the final product is definitely uncomplexed β -HMX of good crystal shape. However, decomposition of the complex needs to be further investigated.

Experimental procedure

Cooling crystallization

Crude, wet HMX was suspended in γ -butyrolactone (30–45 g/100 g lactone) and the mixture was heated to 120°C at 0.2 bar. Most of the water and acetic acid was distilled off and the amount of solvent was adjusted after analysis. When the HMX was completely dissolved the mixture was cooled by a temperature programme. The programme used was dictated by the desired particle size of the product. The crystals obtained were then filtered, thoroughly sucked dry and finally washed with water.

Precipitation

Crude HMX was dissolved in γ -butyrolactone (10–20 g/100 g lactone) at room temperature or higher. The solution was mixed with an equal volume of water in a stirred vessel or a static mixer. The precipitate was filtered off and washed with water. Water and acetic acid were distilled off from the mother liquor and the remaining γ -butyrolactone was reused.

References

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