

ENERGETIC MATERIALS SEPARATIONS AND SPECIFIC POLYMORPH PREPARATIONS VIA THERMAL GRADIENT SUBLIMATION

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ABSTRACT

The principles and methods of thermal gradient sublimation are presented, and experiments showing the application of the technique to energetic materials research are described. Results include the separation of TATB from chlorinated derivatives, the purification of HNAB, and the growth of specific polymorphic forms of HMX and HNAB.

INTRODUCTION

Thermal gradient sublimation is a simple and inexpensive method that may be used for purification or crystal growth when a substrate possesses a reasonable volatility. To achieve purification of a mixture, a sample is sublimed down a progressively cooler thermal gradient, where the components condense in temperature zones that correspond to their vapor pressures. Small structural differences between a mixture's components can lead to significant changes in volatility, so that similar molecules can frequently be separated.

A second application of the technique is the production of specific polymorphic forms of a compound. DSC or other methods can often define temperature ranges where individual polymorphs are thermodynamically stable; by adjusting temperature and pressure conditions in the sublimator unit, a compound may be induced to sublime onto a surface within one of these ranges, selectively forming the desired polymorph. This approach is clearly superior to specific polymorphic syntheses done via solution techniques where parameters such as rate of addition or rate of cooling may need to be closely monitored. Not only is sublimation simpler, but the process also removes any occluded solvent that may have been present in the starting material.

This paper discusses the results of thermal gradient sublimation experiments on the energetic materials TATB, HMX, and HNAB. It is intended to demonstrate the value and versatility of the technique as an analytical method and laboratory tool.

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METHODS

A diagram of a thermal gradient sublimator is shown in Fig. 1. The device consists of a bored aluminum cylinder whose internal heater and cooling coils produce a temperature gradient down the length of the cylinder. A 65-cm long, 12-mm o.d. glass tube containing a powder sample (~ 0.1 g) is inserted into the unit so that the sample rests in the hot end of the sublimator. The maximum temperature is adjusted with a variac, and a vacuum (typically 10^{-3} torr) is applied to the glass tube. The sublimation process is allowed to proceed for one week with continuous pumping, after which time the glass tube is removed and sectioned to recover the products.

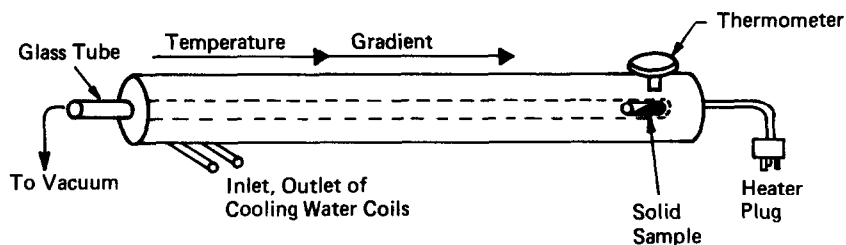


Fig. 1. Diagram of a thermal gradient sublimator unit.

RESULTS

TATB (1, 3, 5-triaminotrinitrobenzene)

TATB is an explosive currently attracting much interest due to its high resistance to initiation. While it has desirable properties from a safety standpoint, its solubility properties are dismal; there is no known solvent in which it has appreciable solubility. Thus, TATB cannot be purified by conventional reprecipitation or preparative chromatographic techniques. However, its marginal volatility makes it amenable to purification by sublimation, and it was found that a maximum gradient temperature of 170°C was sufficient to perform the experiment while minimizing decomposition of the starting material.

A TATB sample obtained from Lawrence Livermore Laboratory (LLL-B592) was sublimed as described above; after one week, two yellow, overlapping bands developed on the tube walls (Fig. 2). Mass spectroscopic analysis of the major band (in the warmer temperature zone) showed that it was TATB. The second band was sampled at its two ends; the zone next to the first band contains a mixture of TATB and a monochloro TATB derivative (X), while the other sample is a mixture of the monochloro derivative (X) and a dichloro derivative (Y). Fig. 3 diagrams the likely structures of X and Y, and shows their similarity to TATB. The isomeric assignments of each were made with the assumption that X and Y are products of the incomplete nitration of 1, 3, 5-trichlorotriaminobenzene during the synthesis of TATB.

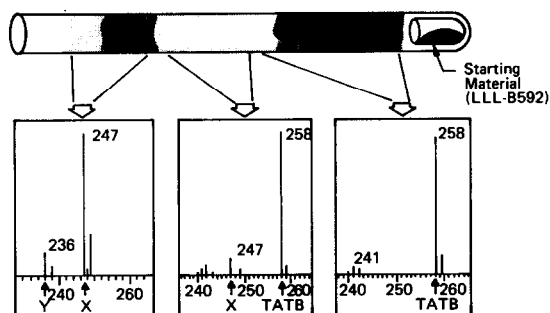


Fig. 2. Diagram representing appearance of glass tube following TATB sublimation and mass spectral analysis of indicated zones.

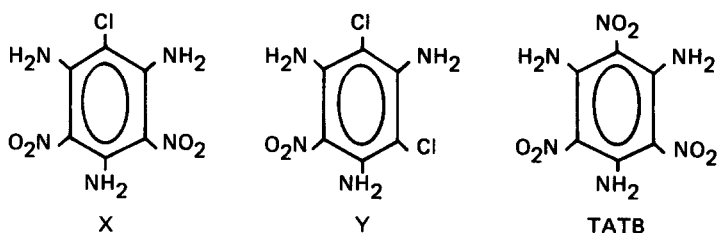


Fig. 3. Structures of x, y, TATB.

"Ultrafine" TATB is a high-purity powder obtained from another source. When ultrafine is subjected to thermal gradient sublimation, a distinct yellow band separates from the TATB band; the former proves to be a monochloro derivative of TATB (Z in Fig. 4). The mass spectrum of Z shows the expected parent peak at 277, and also exhibits a peak at 247. The latter could be interpreted as due to compound X. However, this signal is thought to represent a mass of M-30 (loss of NO), since the mass spectrum of TATB also contains a prominent peak at M-30.

The above experiments show that when TATB is derivatized by replacing either an NH_2 or an NO_2 group by Cl, the resulting species is more volatile than TATB. It also appears that additional chlorine substitution results in increased volatility. Thus it is reasonable to expect that thermal gradient sublimation can separate most chlorinated derivatives from TATB, resulting in a TATB product significantly reduced in chlorine content. Infact, initial results indicate that sublimed ultrafine TATB has a fivefold reduction in chlorine level*, and refinements are expected to improve the figure to a least tenfold.

*% Chlorine before sublimation 0.044, after 0.009. Galbraith Laboratories, Knoxville, Tennessee.

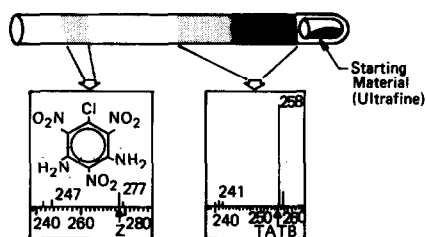


Fig. 4. Diagram showing sublimed compounds from ultrafine TATB and mass spectral results of indicated zones.

HMX (cyclotetramethylene tetranitramine)

There are four known polymorphs of HMX, the alpha, beta, gamma, and delta forms. Previous work has established temperature ranges where each polymorph is thermodynamically stable (ref.1); these are listed in Table 1. When HMX is sublimed onto a cold water (15°C) probe, the temperature of that surface promotes the selective formation of beta-HMX. Similarly, it was found that placing HMX in the thermal gradient sublimator unit with a maximum temperature of 140°C causes crystalline HMX to condense a short distance from the starting material, upon a surface slightly below 140°C. These crystals were shown to be 95+% alpha by both IR and powder pattern tests. The unit may also be adjusted to produce the delta form by subliming HMX onto a surface above 160°, but the reader should be wary of the relative instability of this form.

TABLE 1

Temperature stability ranges for HMX polymorphs

Beta	Below 102°C
Alpha	104° to 160°C
Gamma	Metastable
Delta	164° to melting Pt. (M.P. approx 265°C)

Since gamma-HMX is a metastable allotrope, no method that relies on thermodynamics (such as sublimation) can be used to produce it. It may be prepared by crash precipitation from acetone.

HNAB (2, 2', 4, 4', 6, 6'-hexanitroazobenzene)

There are five known polymorphs of HNAB (ref.2). Forms IV and V are unstable allotropes formed only from the melt on supercooling during recrystallization.

Forms I, II, and III are more accessible, and the DTA of HNAB shows temperature regions where each is thermodynamically stable (Fig. 5). The endotherms at 150° and 180° correspond to the solid + solid transitions I+II and II+III respectively, while the 220° endotherm denotes melting (the irregular area at 190° is thought to represent an impurity).

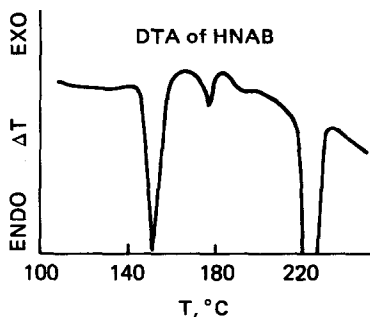


Fig. 5. DTA of HNAB.

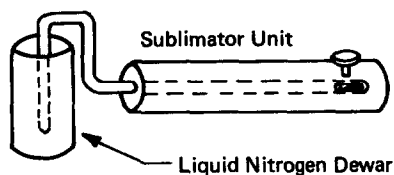


Fig. 6. Diagram of sealed tube with arm in liquid nitrogen for HNAB crystal growth.

The x-ray crystal structures of forms I and II have been previously determined (ref.3). The authors had desired to complete the series with the structure of type III, but encountered difficulty in growing a suitable untwinned crystal. Thermal gradient sublimation has recently been used to achieve this preparation. A glass tube containing HNAB was sealed under vacuum before placing it into a sublimator unit, because the growth of clear, well-formed crystals is promoted by static conditions. The maximum temperature of the gradient was set to 200°C, and, in order to prevent any decomposition gases from increasing the pressure within the tube, an external section of the tube was immersed in liquid nitrogen (Fig. 6) during the week-long sublimation period. These procedures yielded type III crystals of a clarity and size suitable for crystallography; the structure is in progress.

In the course of the sublimation described above, two faint bands (in addition to the HNAB band) developed in the glass tube. An orange band which deposited in the center of the tube was identified as tetranitroazobenzene by mass spectroscopy. A faint yellow band in the coolest region of the tube gives a mass spectrum with a maximum m/e at 371; no structure has been assigned to this material.

REFERENCES

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