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THERMAL STABILITY OF THE CRYSTALLISATION NUCLEANT
2,4,6 trinitrotoluene, TNT, and 2,2',4,4',6,6'hexanitrostilbene, HNS

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Abstract

The 2,2',4,4',6,6'hexanitrostilbene, HNS, nucleant, used in the crystallisation of 2,4,6,trinitrotoluene, TNT, was precipitated from molten TNT and examined by differential scanning calorimetry, DSC, at several stages during purification by vacuum sublimation. During purification a broad endotherm, associated with nucleant decomposition, which could be resolved into two endotherms, depending on the sublimation temperature, was observed. Pure nucleant prepared at 70°C showed a similar behaviour during thermal annealing for extended periods of time at >85°C. Thus TNT, retained in the recrystallised HNS nucleant, may be migrating during the purification process or may occupy a range of lattice sites, which exhibit different activation energies for migration to the surface of the solid during thermal decomposition of the nucleant. Loss of TNT from the nucleant, during purification, could produce some free HNS. The activation energy for nucleant decomposition, which may be a two-stage processes with the initial mobility of the TNT being the limiting reaction, was estimated to be ~210 kJ mol^{-1}. The lattice sites available for the TNT in the host HNS nucleant require elucidation and are the subject of further studies to be published at a later date.

Keywords: crystallisation nucleant, HNS, TNT

Introduction

The widespread use of 2,4,6,trinitrotoluene, TNT, in munition fillings either as a high explosive composition or as an energetic binder for other high melting point explosives, was based on its low melting point, low impact sensitivity and low production cost. Problems associated with its use are well documented as are the practical solutions [1–12] and have been reviewed in earlier publications [13, 14].

Addition of small amounts, ~0.5%, of an almost insoluble material, hexanitrostilbene, HNS, to the mixture produces the optimum number of nucleating

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sites after a double thermal cycle from ambient firstly to 110°C and then to less than 85°C [15]. The second heating cycle above the melting point is required since, the material still supercools after the first heating cycle. This nucleant process improves grain structure orientation and the filling's mechanical properties [10, 11]. Repeated heat cycling through the molten state to <85°C does not destroy the fine grain texture. If the temperature exceeds 90°C the nucleant is destroyed but can be regenerated by heating to >110°C and repeating the Bofors cycle [11].

A 2:1 complex of TNT and HNS, formed as the TNT began to melt during the reheat cycle, has been proposed as the effective nucleant [10, 11]. Nucleant thermal stability depended on the experimental conditions. Pure nucleant decomposed between 85 and 100°C and was not reformed by further heating cycles regardless of temperature [12]. During nucleant decomposition, liquid TNT appears on the surface of the complex. The nucleant is different from either TNT or HNS [16]. The nature of the nucleant, its structure, thermal stability and the conditions, under which it is formed, are unclear. In earlier publications we have investigated nucleant formation in situ and the structure of separated 'pure' nucleant formed from HNS dissolved in molten TNT [13, 14, 17] and have found evidence of production of the nucleant by heating samples with 3% HNS to 170°C. This study was undertaken to examine the nucleant's thermal properties and identify any changes occurring during the purification process.

Experimental

Materials

Details of materials sources and purification processes have been given in earlier papers [13, 14]. All purified samples were vacuum dried at 20°C and 10^{-2} mm Hg for 48 h before use. Material purity was determined by high performance liquid chromatography (HPLC) as described previously [14].

Nucleant preparation and purification

The nucleant was prepared by modified literature methods of hot filtration and vacuum sublimation [11, 13]. 10 g samples of TNT containing 3% HNS were heated to 160°C, in order to dissolve the HNS, then cooled to 85°C and, after 30 min, any separated solid was filtered off on a No. 4 sintered glass disc at 85°C. In further preparations filtration was performed at 95°C and also the TNT was allowed to set and remelted at 85°C before filtering. Samples of powdered crude nucleant were purified, from excess TNT, by vacuum sublimation, 10^{-2} mm Hg 70°C, with liquid nitrogen as the condensing agent, until no further material collected on the cold finger and the DSC curve showed no evidence of the normal TNT melting endotherm. The effect of sublimation temperature on nucleant composition was investigated by a repeat preparation using vacuum sublimation at 85°C.

Thermal analysis experiments

DSC experiments were performed on samples in the 4 to 30 mg range using a Mettler TA 4000 apparatus with a DSC 30 chamber connected to a TC 11 TA Processor. Output was to a Hewlett Packard Colourpro plotter. Alumina in a sealed aluminium crucible or an empty crucible was used as the reference sample. An approximate value for nucleant composition was obtained by comparing the TNT fusion enthalpies, before and after nucleant decomposition with a TNT standard using the DSC integrating program. Differences between the mass of TNT calculated from the endotherms and the mass of nucleant was assumed to be HNS. Variations in the fusion enthalpy with cycling can indicate a mass loss or a change of state. DSC curves of nucleant samples, taken at several stages during the purification process, were recorded between ambient and 130°C. Crude nucleant filtered off at 95°C was also examined by DSC. Measurements were performed on samples of pure nucleant, which had been thermally annealed in the DSC for times between 10 and 60 min at temperatures between 85 and 100°C, cooled to ambient, prior to recording the normal measurements from ambient to 130°C.

Results and discussion

The DSC curves obtained with nucleant samples filtered off from molten TNT at 85°C are shown in Fig. 1. Removal of the excess TNT from the crude nucleant, Fig. 1(a), during purification by vacuum sublimation, results in a change of shape of the endotherm associated with the nucleant TNT material Fig. 1(b) to (d). For samples sublimed at 85°C, during the purification the nucleant endotherm splits into two distinct endotherms with maxima at 108 and 115°C Figs 1(b) and (c). The relative proportion of free to nucleant TNT decreases and the ratio of the 115 to 108°C endotherms increases (Tables 1 and 2). Even when the purification is performed at 70°C there is evidence, Fig. 1(d), for a second component to the endotherm. These observations indicate that either there are at least two different lattice sites for TNT in the nucleant or that migration of TNT in the lattice is a two-stage process. If the nucleant is a solid solution of TNT in a recrystallised HNS lattice then, TNT close to the surface of the mixed crystals would show higher mobility and could require a lower activation energy, indicated by the lower temperature peak, for migration to the surface to join the bulk of the free TNT, which is being removed by the sublimation process. When all the free TNT has been removed the only observed

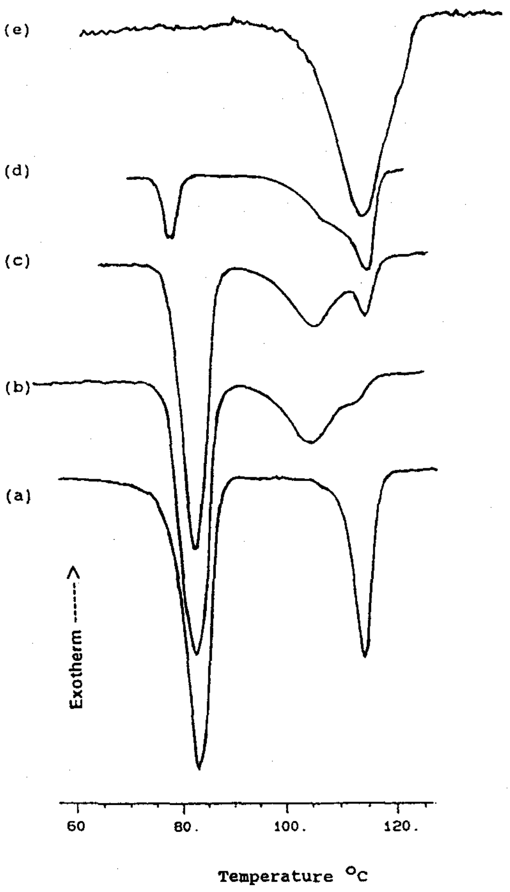

Fig. 1 DSC curves of nucleant during purification (a) as filtered at 85°C, (b) after sublimation at 85°C for 6 h, (c) after sublimation at 85°C for 12 h, (d) and (e) after sublimation at 70°C for 6 h and 12 h respectively. All measurements performed at 20°C min^{-1} heating rate

endotherm, associated with the nucleant, should be from the more stable species, Fig. 1(e). TNT molecules replacing HNS molecules in the lattice would be essentially occluded from the sublimation process and require a higher activation energy for migration than the surface TNT. In earlier publications we have shown that the nucleant lattice is different from the normal HNS lattice [16, 17] and hence the activation energy for migration will be different from the normal HNS lattice.

When nucleant, filtered off at 85°C and purified by sublimation at 70°C, is annealed at temperatures above 85°C then, the nucleant endotherm shows similar modifications to that observed during the purification process at 85°C, with a broadening of the endotherm, Figs 2(a) to (d), and a slow conversion of nu-

Table 1 Measured thermal values for nucleant samples during preparation and purification

Sample	Treatment temperature/°C			Peak areas/mJ		Masses/mg			Mass ratios		Mole ratio
	Filt.	Subl.	Time/ h	Free TNT	Nucleant TNT	TNT f	TNT n	HNS	$\frac{TNT_f}{TNT_n}$	$\frac{TNT_n}{HNS}$	$\frac{TNT}{HNS}$
Crude Nucleant	85			942	409	6.10	2.60	4.40	2.35	0.59	1.19
Crude Nucleant	95			246	108	1.59	0.27	0.74	5.89	0.37	0.72
Crude Nucleant	85	85	2	949	544	6.10	3.50	13.30	1.74	0.26	0.51
Crude Nucleant	85	85	12	25	520	0.16	3.36	16.70	0.05	0.20	0.39
Pure Nucleant	85	70	24		545		3.52	6.22		0.57	1.12
Pure Nucleant	85	70	24		503		3.27	5.26		0.62	1.22
Pure Nucleant	95	70	24		352		2.35	7.56		0.31	0.62
Pure Nucleant	95	85	24		520		3.46	16.74		0.21	0.42

Calculations assume molar enthalpies of melting for nucleant TNT and free TNT are equal. Columns labelled 'f' and 'n' denote free and nucleant TNT respectively. Difference between sample mass and calculated TNT mass is mass of HNS in nucleant i. e. No free HNS

Table 2 Redistribution of TNT in nucleant during purification at 85°C

Treatment time/ h	Peak areas			Ratio	Ratio
	TNT free	Nucleant 1	Nucleant 2	$\frac{TNT_f}{TNT_n}$	$\frac{Nuc_1}{Nuc_2}$
0	942	409		2.310	
3	1425	506	99	0.055	5.31
6	949	333	147	0.290	2.26
12	5	520		0.009	–
0*	0	62	10		6.20

Nucleant 1 is associated with the 107°C endotherm and nucleant 2 with the 115°C endotherm but the pure nucleant only shows a single peak. The subscripts f and n denote free and nucleant TNT. All samples are nucleant separated at 85°C and purified at 85°C excepr for the zero time* material which is nucleant purified at 70°C and measured at 5°C min^{-1} heating rate

cleant TNT to non-nucleant TNT (Table 3). The distribution of TNT between the free state and the two possible nucleant species, after annealing, is a function of the heating rate, Figs 3(a) to (d). Some additional annealing may be occurring during the measurement. Results indicate an annealing onset temperature of ~85°C, Fig. 2(a), and at a 5°C min^{-1} heating rate the sample will be effectively annealed for an additional five minutes before the onset of the decomposition endotherm. Also the peak temperatures are lower for lower heating rates. Pure nucleant heated at 5°C min^{-1} also shows some evidence of endotherm splitting, Fig. 3(d).

Annealing of nucleant, purified at 70°C, for one hour at 100°C produces a small residual nucleant endotherm, Fig.4(a). The composition of this mixture is similar to that for which a nucleant endotherm can be produced by repeated thermal cycling [16], and hence an equilibrium concentration of nucleant, which may not be annealed at this temperature, could remain in the HNS lattice. Further work on annealing of the HNS lattice is required to determine if, after nucleant is decomposed, the normal HNS lattice is regained. Repeat heating of a sample filtered at 95°C, which contains less TNT, Fig. 4(b), shows no evidence of the nucleant endotherm after the first heating cycle Fig. 4(b).

The composition of crude nucleant, prepared from the same original 3% HNS in TNT melt at 160°C, is a function of filtration temperature. At 85°C, the mass ratio nucleant TNT:HNS is 0.57 but at 95°C the ratio is only 0.099. When the nucleant is purified by sublimation at 85°C there is also a reduction in the TNT:HNS ratio in the nucleant Table 3. The X-ray powder pattern of this material is ill defined and does not match the pattern obtained from the 70°C purification. The particle size of the powdered crude nucleant, prior to sublimation, may influence the speed of the purification and composition of the product for sublimation at 70°C if there is any decomposition of nucleant during purification. This effect would be reduced at 85°C, above the melting point of the free

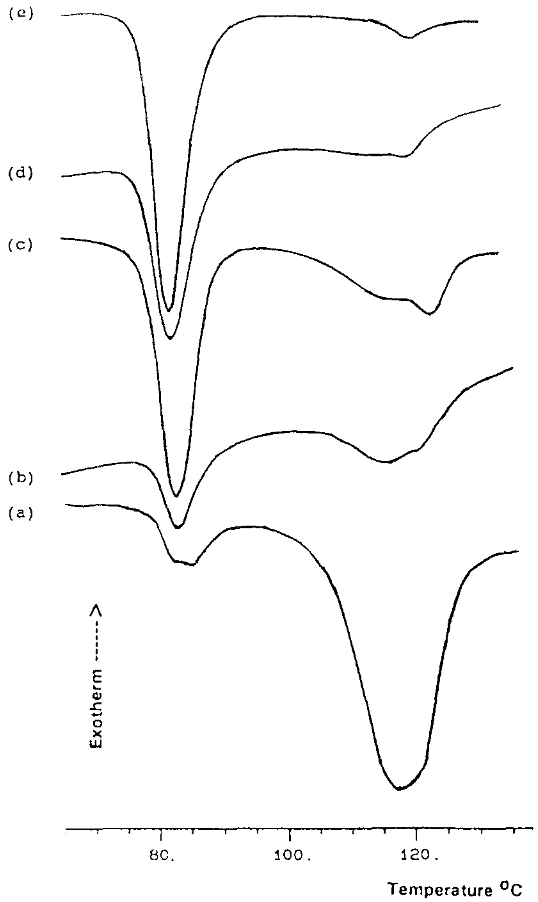

Fig. 2 DSC curves of nucleant following annealing treatment (a) 10 min at 85°C, (b) 15 min 95°C, (c) 30 min at 95°C, (d) 45 min at 95°C, (d) 60 min at 100°C

TNT. Crude nucleant particle size was not controlled in any way, since the filtered material was broken up and gently ground in an agate pestle and mortar prior to the purification. It is difficult to ascertain from the data given in Table 1 if the sublimation at 70°C is removing nucleant TNT since the difference in TNT:HNS mole ratio between the crude filtered nucleant and the pure material is similar to the composition difference for repeat samples purified under nominally the same conditions.

If the nucleant was a complex of the form TNT_2HNS then the amount of HNS in the complex isolated at 95°C would be 10% of the total HNS present i.e. 90% of the HNS would be in the normal crystal form. Either the nucleant is formed first and pure HNS is then precipitated on the nucleant nuclei or pure HNS is formed first and the nucleant is then deposited during the final stages.

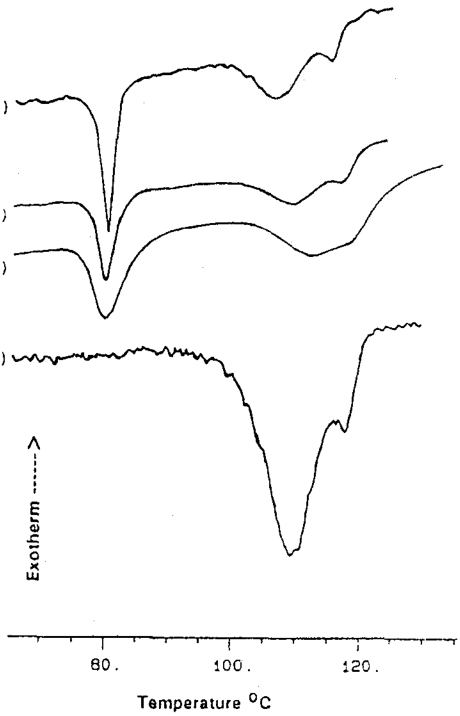

Fig. 3 Effect of heating rate on DSC curves obtained from (a) untreated pure nucleant, 5°C min^{-1}, (b) (c) and (d) nucleant annealed for 15 min at 95°C and heating rates of 20, 10 and 5°C min^{-1}, respectively

The latter is unlikely since the annealing studies, described below, show the nucleant is unstable with respect to HNS and free TNT at 95°C. The formation of pure HNS on the nucleant does not appear feasible since the X-ray powder pattern from the precipitate after removal of excess TNT does not correspond to either of the known crystal forms of HNS [18, 19]. Therefore the nucleant is probably a solid solution of TNT in recrystallised HNS with variation in composition dependent on precipitation and purification conditions. The increased mobility of TNT in HNS at the higher filtration temperature, which is above annealing onset, would be expected to increase the amount of free TNT, some of which would be removed in the filtration stage. Perhaps a low temperature solvent removal of the excess TNT as previously suggested [12] would yield a different product, although simple washing of the crude material on the sintered disc with acetone at ambient for <1 min removed all traces of nucleant endotherm, Fig. 4(d), as found previously [9].

The nucleant decomposition temperature, 115°C, is about 2/3 of the melting point of HNS, 321°C, which is the normal condition for defects in solid lattices to become mobile and migrate through the lattice. This mechanism may allow the trapped TNT to migrate to the surface and possibly allow the HNS lattice to

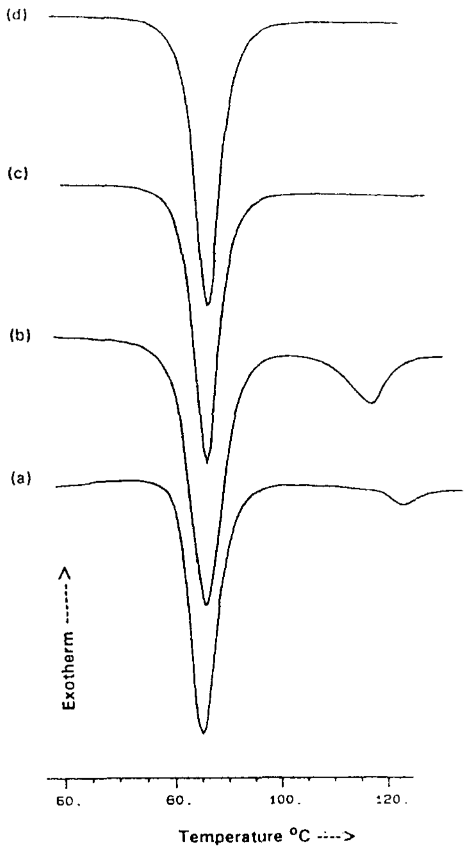

Fig. 4 (a) Nucleant filtered at 85°C and sublimed at 70°C after 1 h anneal at 100°C, (b) Nucleant filtered at 95°C, (c) repeat heating of sample (b), (d) nucleant filtered off at 85°C and washed with acetone for 1 min at RT

recover its normal structure. The energy of formation of a vacancy in a molecular crystal is large and compares with the enthalpy of sublimation [20]. Simple vacancy concentrations are quite low as the temperature approaches the melting point [21], however for dipolar molecules with rotational options i.e. TNT with NO_2 groups twisted out of the plane of the aromatic ring, then the movement of molecules for vacancy formation will be easier. Growth defects in HNS containing TNT will be high and the movement of the TNT via a dislocation/vacancy generation mechanism could be facile. Calculation of the activation enthalpy for molecular migration is difficult since the migration will be strongly dependent on lattice direction due to the highly planar nature of the lattice. Movement along the planes will be easier than movement across the planes unless there is a dislocation present to assist the migration. When solid solutions are formed then diffusion is easier than for pure compounds [22]. Further work on the mobility of impurities within the HNS lattice is in progress.

Table 3 Redistribution of TNT in Annealed Nucleant Samples

Treatment time/ min	T/ °C	Peak areas			Ratio	Ratio
		TNT free	Nucleant 1	Nucleant 2	$\frac{TNT_f}{TNT_n}$	$\frac{Nuc_1}{Nuc_2}$
0		0	545		0	–
30	85	10	158	25	0.055	6.3
45	90	44	127	24	0.290	5.3
10	95	48	119	28	0.326	4.3
15	95	32	36	10	0.864	3.6
30	95	219	55	66	1.81	0.85
45	95	100	12	14	3.85	0.85
60	100	71	3		24.0	
10 PN2	100	82				

All samples are nucleant separated at 85°C and purified at 70°C except for PN2 which was separated at 95°C. The subscript f and n denote free and nucleant, respectively.
Nucleant 1 is associated with the 107°C endotherm and nucleant 2 with the 115°C endotherm

Activation energy for nucleant decomposition

The activation energy for the change from nucleant to a mixture of TNT and HNS was determined from the variation of the rate of conversion with temperature. Plots of the mole fraction of nucleant and free TNT, calculated from the peak areas, as a function of time at 95°C were straight lines, see Fig. 5, indicating a simple first order process. According to the Arrhenius equation [23]

$$\ln k = -\blacktriangle H/RT + C$$

Where k is the rate constant for the reaction, $\blacktriangle H$ the enthalpy of reaction and R the gas constant. $\blacktriangle H/R$ can be calculated from the slope of the plot of $\ln k$ *vs.* $1/T$. The rate constant, k, was determined from the annealing curves at 85 and 95°C, after correction for the time taken to reach the annealing temperature [24]. The activation energy, determined from the data in Table 3, using the combined endotherms at 108 and 115°C as the measure of the nucleant TNT concentration, was 210 kJ mol^{-1}. This value is similar to the migration energy for solid solutions in organic materials [25]. The two nucleant endotherms at 108 and 115°C were insufficiently resolved to enable the kinetics and hence the activation energy for the interconversion between the two possible TNT species to be determined.

Previous X-ray studies [17] on the nucleant has shown it to have different crystal parameters from normal HNS and there is no evidence for the existence of a separate crystallite of TNT within the HNS structure. Hence the crystal

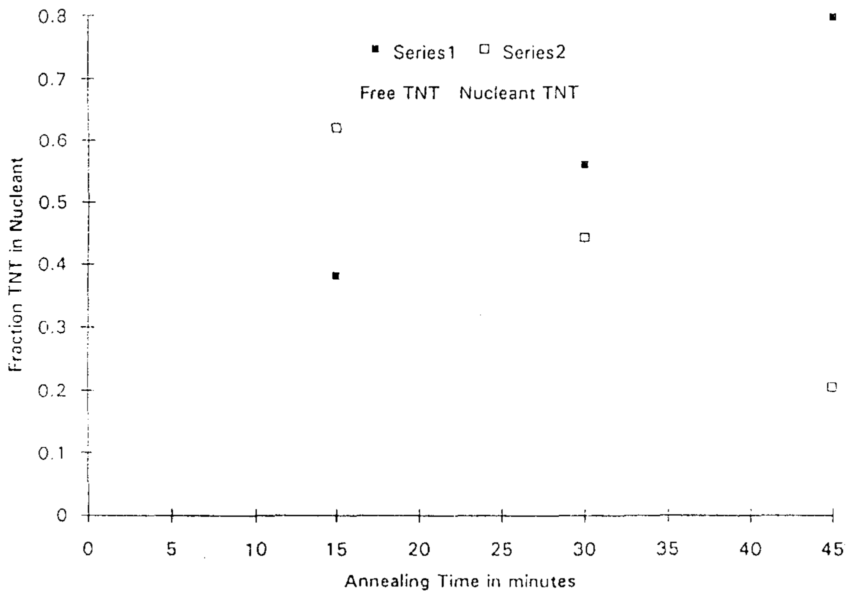

Fig. 5 Mole fraction of free and nucleant TNT against annealing time at 95°C

form of the TNT, either monoclinic or orthorhombic [26, 27] does not arise. This observation would fit the solid solution hypothesis as well as the TNT and HNS complex formation theory. TNT migration, as evidenced here supports the solid solution proposal and not complex formation. The molecular structure of the TNT included in the HNS may be different from either of the two molecular forms present in both normal crystal forms. The rotation of the TNT nitro groups, with respect to the aromatic ring, may be different in the mixed TNT/HNS lattice compared to the normal TNT lattice, in order to accommodate the additional hydrogens of the TNT methyl group. Further work on this aspect will be published in future communications.

Conclusions

Thermal methods have shown that TNT contained within the HNS nucleant, formed from the recrystallisation of the HNS from molten TNT, is not present in a single form but can occupy a series of different sites with different activation energies for migration. Thermal treatment of the purified nucleant below the decomposition temperature causes a redistribution of the TNT in the solid. Nucleant decomposition occurs with an activation energy of 210 kJ mol^{-1}, at temperatures, which correspond with the expected mobility of lattice defects in the HNS lattice.

Nucleant purification by vacuum sublimation should be performed at the lowest temperature and highest vacuum possible to minimise the migration of the TNT out of the nucleant. The initial temperature for separation by filtration is less important whilst there is an excess of TNT inhibiting the diffusion but as the excess is removed the temperature should be reduced to close to the TNT melting point.

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