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Polymorphism in 2,4,6-Trinitrotoluene Crystallized from Solution

Ranko M. Vrcelj,[†] **Hugh G. Gallagher,**[‡] **and John N. Sherwood***[,†]

Contribution from the Department of Pure and Applied Chemistry and Department of Physics and Applied Physics, University of Strathclyde, Glasgow G1 1XL, Scotland, UK

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Abstract: An examination has been made of the role of solvent type in the definition of the polymorphic nature of 2,4,6-trinitrotoluene precipitated from solution. A combination of calorimetric and structural techniques including in situ crystallization studies using synchrotron radiation has shown that the variations in polymorphic form following precipitation from solution do not arise specifically from any stereospecific guidance that the nature of the solvent might impose on the structural form. Rather the differences are linked to the variations in solubility and hence supersaturation which might build up prior to nucleation and growth and to the isolation of the metastable orthorhombic phase from the solvent. The final conclusion is that the changes fit well with Ostwald's Law of Stages with the orthorhombic form always precipitating initially followed by its conversion to the stable monoclinic form. The previously observed tendency for some solvents to yield one or the other form then becomes attributable to kinetics in solution rather than structural control. It can be associated with the solubility of the material in the solvent used and the role of this factor in a solvent-mediated phase transformation. On this basis rules can be formulated for the isolation of the metastable forms of this and similarly related polymorphic systems.

Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most commonly used explosives in the modern world. Although its chemistry has been studied extensively by a variety of means,[1−8] its structural forms have only been elucidated relatively recently.[9−12] These recent studies have confirmed the existence of two crystallographic forms, monoclinic and orthorhombic (Table 1), and have clarified the confusion that existed in much of the earlier work on phase relationships in this material. They show that the basis of the polymorphism is a small change in molecular conformation and packing which allows that resulting change in structure. From this starting point, Gallagher and Sherwood[13] made a detailed examination of the monoclinic form showing that this can develop a highly faulted structure of twins and stacking faults. The degree of the faulting was shown to depend on the nature of the growth process and on the rate of the growth of the material: fast, most defective, and slow, most perfect. They also demonstrated that the polymorphic nature of the product could be changed by varying the solvent used for growth. Some of the solvents used yielded the monoclinic form while others gave the orthorhombic form. Structural considerations revealed that the twinning and faulting of the monoclinic structure could arise by the formation of a pseudo-orthorhombic structure at the twin or stacking fault boundary. This indicates a close structural and energetic relationship between the two polymorphs and hence the potential for their easy interconversion or direction during formation. A theoretical examination[14] confirmed a small difference in lattice energy between the monoclinic (−28.78 kcal mol^{-1}),[15] twinned monoclinic (−28.43 kcal mol^{-1}), and orthorhombic (−28.24 kcal mol^{-1}) forms.

Table 1. Crystallographic Data for TNT

parameter	monoclinic	orthorhombic
a (nm)	2.1275	1.5005
b (nm)	0.6093	2.0024
c (nm)	1.5025	0.6107
β (deg)	110.23	90
Z	8	8
space group	$P2_1/c$	$Pb2_1a$

The current interest in the possibility of engineering the polymorphic nature of materials gives a system of this type some importance.[16,17] With such a close relationship and ready interchange between the molecular and structural components by which the overall structure is defined, TNT could well serve as a test medium for learning how control could be imposed to yield one form or the other. To this end we have extended our

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[*] To whom correspondence should be addressed.

[†] Department of Pure and Applied Chemistry.

[‡] Department of Physics and Applied Physics.

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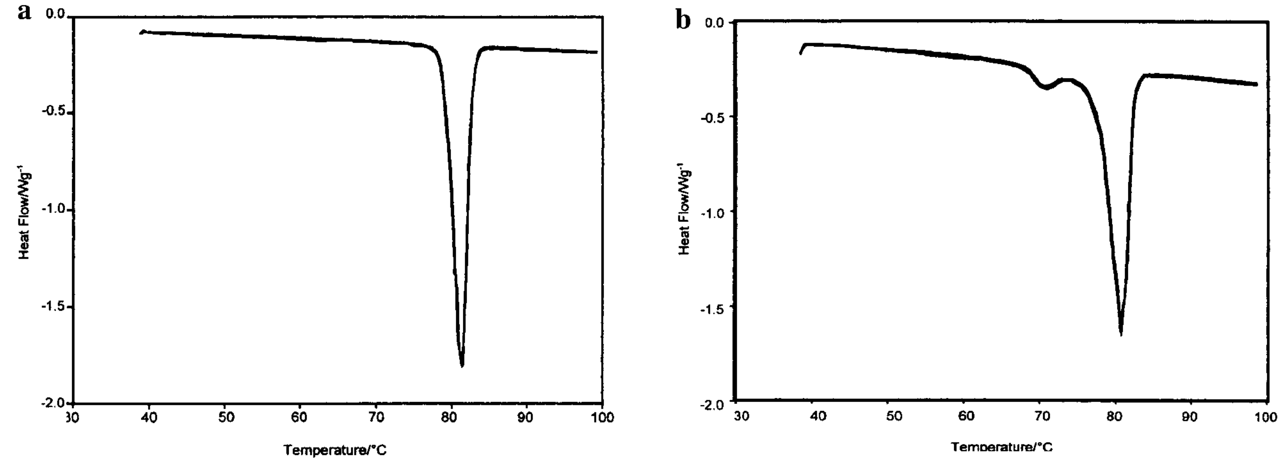

Figure 1. DSC traces for (a) monoclinic and (b) orthorhombic TNT.

studies of this material to attempt to define the basis of the growth and transformation process through a detailed examination of the role of solvent and solubility in the definition of the polymorphic nature of TNT precipitated from solution. As with many materials that exhibit polymorphism, accurate solubility data only exist for one form, the stable monoclinic, though in a variety of solvents.[13,18] No measure of the solubility of orthorhombic TNT or its relationship to that of monoclinic TNT is available for any of the solvents used. However, on the basis of the close energetic similarity of the two forms, we assume that the solubilities will be equally similar. An ideal solubility[19] can be calculated for monoclinic TNT (after Davey et al.)[17] and compared with those measured for the variety of solvents.[13,18] These calculations show that for TNT none of the solvents used can be thought of as "ideal", indeed they appear to have solubilities an order of magnitude greater or less than the calculated ideal. Clearly for the orthorhombic form, no such ideal solubility curve can be calculated—as yet there have been no reports of a melting temperature or enthalpy of melting for this polymorph.

Experimental Section

The TNT used in this study was supplied by the UK Ministry of Defence as standard military grade in wetted powder form. Prior to use, the material was purified by the method of Gey et al.[20] to remove manufacturing byproduct impurities. The final purity was confirmed as $>$99.99% by gas−liquid chromatography.

Crystallization from solution was carried out in one of two ways: cooling and dilution. **(a) Cooling:** Solutions saturated with monoclinic TNT at 298 K in a range of solvents of differing chemical nature were cooled rapidly by dropping the solution into a chilled metal jacket surrounded by either iced water (273K) or liquid nitrogen (77 K). This resulted in rapid precipitation of the solid and, in the latter case, the eventual freezing of the remaining solution. The frozen liquid was rapidly melted and the solid TNT filtered off at low temperature to arrest any potential conversion of the polymorph formed. The rate of cooling under these conditions was measured to be 15 K min^{-1} for the case of ice and $>$100 K min^{-1} for liquid nitrogen. **(b) Dilution:** To solutions saturated in a range of solvents was added a sufficient volume of water to yield a significant decrease in solubility and hence cause a sudden precipitation of the TNT. Two sets of experiments were carried out using additions of 100 mL of water to 20 mL of solution and 20 mL of water to 20 mL of solution. The solid precipitate was separated from the residual solution and dried rapidly. The residence period in contact with the solution varied during the course of the investigation from the time taken to achieve full precipitation in the earlier stages ($\sim$1 h, slow separation time) to as immediate as possible in the later stages ($\sim$10 s, fast separation time). The differences noted in the composition of the samples separated under these different conditions proved to be important in the analysis of the data.

Differential Scanning Calorimetry. Thermal assessment of the temperature dependence of the phase behavior of the precipitated TNT was made using a DuPont 9900 Differential Scanning Calorimeter at heating rates in the range from 1 to 10 K min^{-1}.

Structural Analysis. Powder diffraction patterns were collected on a modified Siemens Texture Camera using a Bragg−Brentano geometry and nickel-filtered Cu $K\alpha$ radiation. High-resolution powder diffraction (HRPD) was performed on station 9.1 of the Synchrotron Radiation Source (SRS), Daresbury Laboratory, using a wavelength $\lambda = 1.5$ Å in the Debye−Scherrer mode. Energy Dispersive X-ray Powder Diffraction (EDD) was performed on station 16.4 of the SRS. The geometry used was the standard single post sample slit design.[21] The scattering angle was selected to be 1.5° and the photon energy spectrum ranged between 0 and 150 keV. For in situ work, a precipitation cell designed and provided by Daresbury laboratory was used with the precipitation conditions described above.[22] A vial containing the saturated solution was placed in the beam in a position which ensured that the diffraction lozenge resided within the sample volume. An initial data collection was made to ensure that no preliminary crystallization had taken place. Once this had been confirmed, the known volume of water was injected into the solution in the vial by using a compressed gas system. Data sets were then collected as a function of time. Throughout the experimental period the solution was stirred magnetically at a rate sufficient to give an even dispersion of the precipitated solid.

Results

Monoclinic and orthorhombic TNT are easily distinguished (Figure 1a,b) by DSC. Monoclinic TNT shows no features in the trace other than the melting exotherm at 355 K. In contrast, the orthorhombic polymorph exhibits a small exothermic peak at 345 K with a slightly suppressed melting point at 354 K.

Figure 2a,b shows the predicted X-ray powder diffraction patterns of the two forms. It provides a measure of distinction that can be made between the monoclinic and orthorhombic solid using this technique. It is obvious that a parallel lower resolution distinction can be made with EDD. The powder techniques do not allow us to define the possible existence or absence of the twinned monoclinic form defined in our previous

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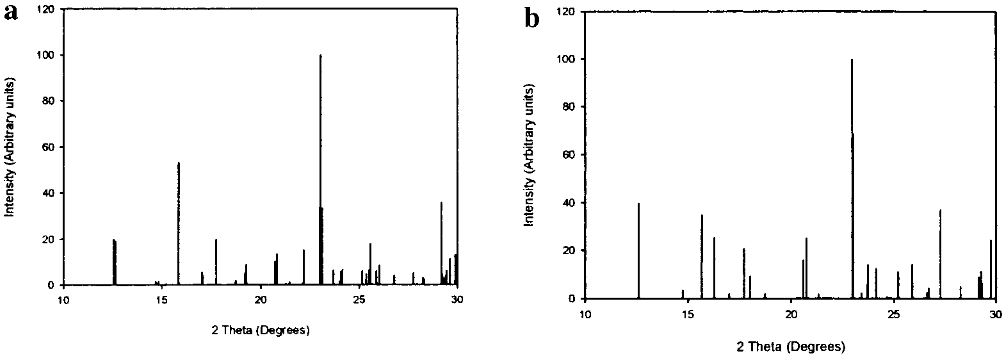

Figure 2. Predicted powder diffraction traces for (a) monoclinic and (b) orthorhombic TNT.

Table 2. Summary of Cooling and Precipitation Data[a]

solvent	solubility	SXD[13]	cooling 15 K min^{-1}	cooling 100 K min^{-1}	precipitation 1:1 dilution			precipitation 5:1 dilution		
					solubility	S	F	solubility	S	F
acetone	110	M	M	M	55	M	M&O	19	M	M&O
ethyl acetate	47	M	M	M	23	M	M&O	8	M	M&O
acetic acid	20	M	M	M	10	M&O	M&O	3	M&O	M&O
methanol	3	M	M	M	1.5	M&O	M&O	0.5	M&O	M&O
ethanol	1	M&O	M&O	M&O	0.5	M&O	M&O	0.2	M&O	M&O
cyclohexanol	<1	O								

[a] Solubilities in weight % at 293 K. S = slow separation time (1 h). F = fast separation time (~10 s). SXD = single-crystal diffraction on samples grown over long periods (weeks).[13]

study. The relative solubilities of the TNT in the original solvents and those formed by the addition of the water are given in Table 2.

Cooling Experiments. The starting point of our examination was the previous work of Gallagher and Sherwood,[14] which examined a wide range of solvent types and provided evidence of a potential link between the nature of the solvent and the polymorphic nature of TNT. The principal aim of that study was to grow large single crystals for X-ray topographic analysis. The crystals were therefore grown by solvent evaporation over periods of several weeks. Under these conditions it seemed likely that any phase transformation would have been completed within the time scale of the growth, particularly with two so closely structurally related polymorphs. As can be seen from Table 2 (column SXD), this procedure resulted in the nucleation and growth of the monoclinic form from the complex solvents at the head of the list while ethanol gave a mix of orthorhombic and monoclinic forms. At the extreme, crystals of only orthorhombic form were obtained from cyclohexanol. As noted in our previous paper, these crystals were stable in the medium term, converting to the monoclinic form over very long periods of time (months). This defines the metastability of this phase and its enantiotropic relationship with the monoclinic form. These previous results were confirmed by the present more rapid cooling experiments. (However, due to the very poor solubility of TNT in cyclohexanol, it proved impossible to perform the precipitation and rapid cooling experiments for this solvent.) As Table 2 shows (columns cooling), DSC analysis of the precipitated material demonstrates the same distinction between the solvents as recognized previously, whether high or low cooling rates are used.

These data, together with a consideration of the relative solubilities of the material, suggest several alternatives: (a) The solvent has a directing influence on the formation of the polymorph. The nature of the product depends on the state of the molecule in solution as defined by solute−solvent interactions. (b) Rapid precipitation yields the metastable form with rapidity being defined to some extent by the relative change in solubility achieved during the process as well as the temperature differential. (c) Whichever is the cause, and since the kinetics of dissolution and transport are slow, the persistence of the metastable form depends on its solubility which will be a dominant factor in any possible solvent-mediated phase transformation to the stable state.

Precipitation Experiments

In the initial stages of these experiments, and to facilitate the analysis in those cases in which the solubility and hence the yield of the product was low, the precipitate was allowed to stay in contact with solution for extended periods (ca. 3−4 h). The aim was to maximize the yield of the product. Under these circumstances, the previous data were almost replicated for both sets of experiment. The particular and reproducible distinction was that crystallization from methanol and acetic acid also yielded the orthorhombic form. Whether or not these conditions reflect an increased precipitation rate is arguable but is of little consequence since repetition of the experiments with the more rapid separation of the product yielded the detection of both polymorphic forms in all of the crystallized products.

Figure 3 shows a powder diffraction pattern of TNT precipitated from acetone. This is a high supersaturation case, but the precipitate was recovered after 10 s. It shows clearly a mix of both phases of TNT. These observations led to the conclusion that the principal course of the events was the formation of the metastable form under all circumstances followed by its conversion to the stable form by a solvent-mediated process. The final confirmation of this conclusion came from the two in situ studies that we were able to carry out.

In situ EDD was limited by two factors. Since significant amounts of material (equivalent to a solubility in solution of >10%) are required in order that the process can be detected at an early stage, the experiments were limited to the more soluble solvents. The time allotted to us for these experiments allowed a complete examination of only two systems. Of the possible experiments the extremes of acetone and acetic acid were chosen.

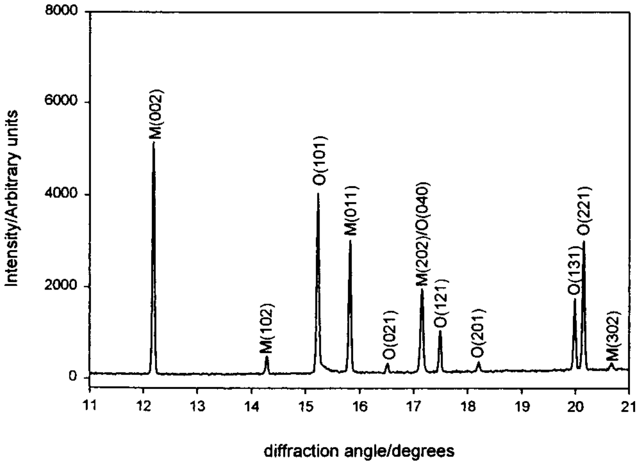

Figure 3. Powder diffraction trace of TNT precipitated from acetone under conditions of high supersaturation and a fast recovery time.

Table 3. Crystallization Existence and Onset Times in Acetone and Acetic Acid Solutions of the Orthorhombic (O) and Monoclinic (M) Phases of TNT

acetone/water (vol ratio)	solubility (wt %)	existence of O (min)	onset for M (min)
47/53	52	0−10	immediate
51/49	56	0−30	>25
56/44	62	0−50	>50
61/39	67	0−60	>60
69/31	76	10−90	>90
acetic acid/water (vol ratio)	**solubility (wt %)**	**existence of O (min)**	**onset for M (min)**
55/45	11	0−20	immediate
64/36	13	0−40	>45
76/24	15	0−60	>60
83/17	17	0−75	>75
90/10	18	>30	not seen

Figure 4a,b, which shows the formation and conversion of the polymorphs, provides a remarkable amount of information on the process. Both cases show strong diffuse backgrounds due to scatter from the solution, which is always found within the diffraction lozenge of such a mixed system. This is unlike cases of crystallization from the melt or by chemical reaction, where disordered material contributing to the background scatter eventually transforms. In growth from solution the solvent yields a constant background. The relative solubilities of TNT in acetone and acetic acid can be qualitatively seen in these traces, and the diffraction intensities of TNT in acetone are greater than those of TNT crystallizing from acetic acid, mirroring the greater solubility of TNT in acetone. In both systems the initial formation of the orthorhombic phase and its change to the monoclinic form can be seen. While the former is just recognizable in the product from the earlier stages of crystallization of the acetone solution, its presence is well-defined in that from acetic acid. In the former case, the time from initial observation of the orthorhombic form to its disappearance (a lower detection limit of ∼5%) is ca. 30 min and the monoclinic form appears after 30 min. In the equivalent case for acetic acid, the orthorhombic phase exists for a longer period of time (∼45 min) and the monoclinic phase begins to grow later (∼50 min). Although these two cases are similar, over the range of dilutions it is clear (Table 3) that slight changes in the volume ratio of the acetone solution bring about large changes in the crystallization behavior of the TNT, while larger changes in the volume ratio for acetic acid are required to generate similar changes. This behavior reflects changes in supersaturation. For acetone, small volume changes bring about larger changes in supersaturation while for acetic acid larger changes are required to produce the equivalent effect. These effects follow Ostwald's Rule of Stages, but the reason that they are visible in this case is that the inevitable lower solubility in aqueous solution effectively isolates the crystallites, slowing transport between the two phases for a short period of time.

As noted previously, no data for the solubility of the orthorhombic form are available. The difficulty in determining accurate data is defined by the EDD plots. There is a very rapid phase transformation from the orthorhombic form into that of the monoclinic. For any accurate and precise measurement of the solubility, the time needed for equilibration in a solubility assessment (∼24 h) would be far longer than the time needed for the metastable phase to transform into the most stable (a few hours at most) at medium to high solubilities.

The development of the EDD patterns should allow an assessment of the kinetics of the transformation process. This is limited by two factors. The first is the lack of suitable models for growth via precipitation from solution and the variable nature of the development of individual X-ray reflections. Some peaks show a well-defined simple power law behavior of the form $x = kt^n$, but with different peaks yielding different exponents, e.g., the $(31\bar{1})$ peak at 51.9 keV (Figure 5a) with exponent 3, and the (602) peak (at 88.4 keV) with exponent 1.5. However, whether such values are meaningful or even if there is a physical

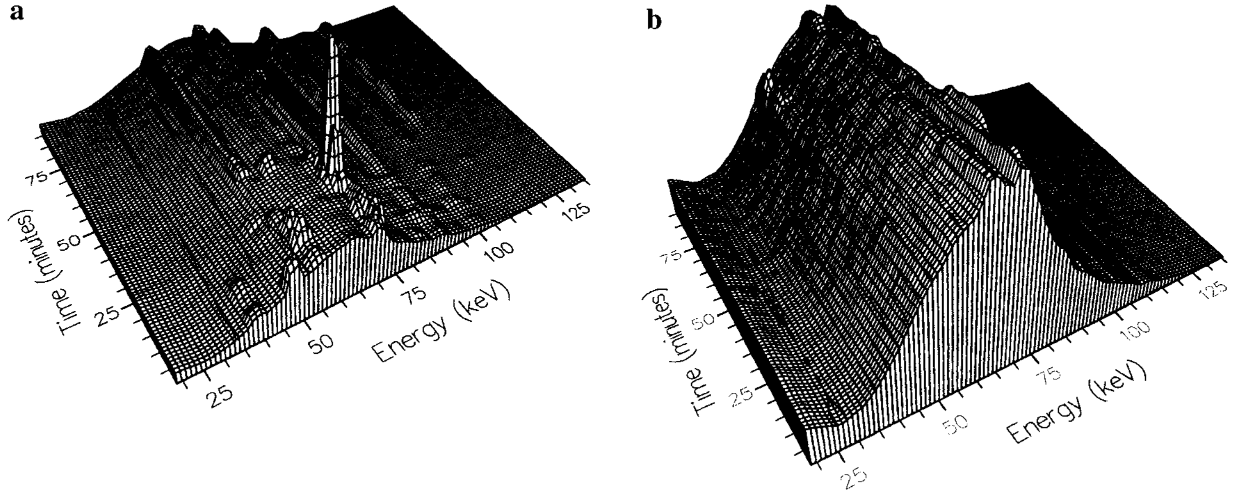

Figure 4. EDD traces of TNT precipitating from (a) acetone and (b) acetic acid.

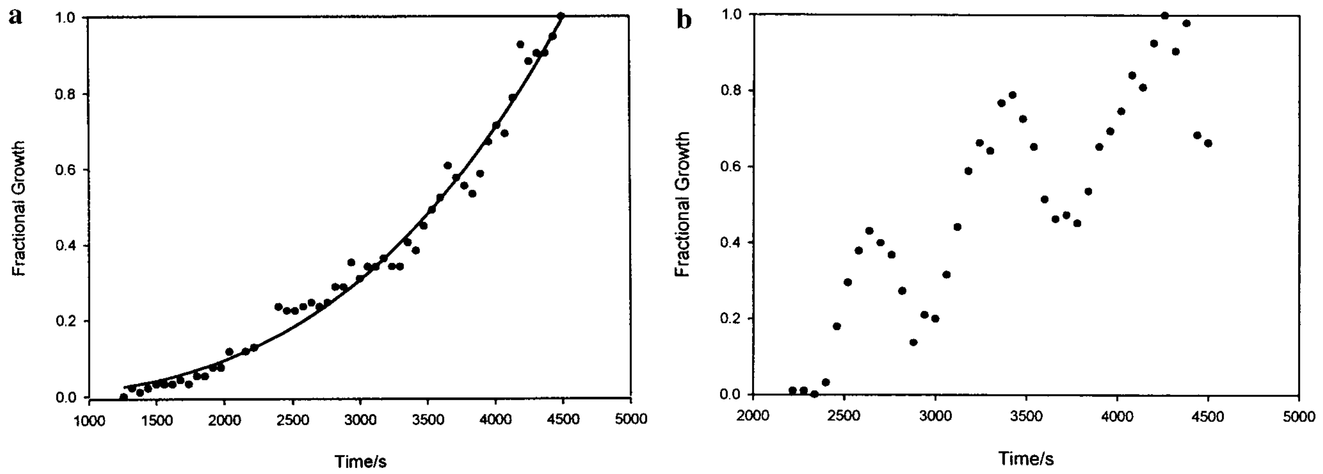

Figure 5. Growth curves for (a) $(31\bar{1})$ at 51.9 keV and (b) (224) at 109.4 keV diffraction peaks.

basis for using such models is still a matter for much debate. Other peaks, e.g., the (224) peak at 109.4 keV (Figure 5b), show an interesting cyclical behavior. The reason for such a cyclical variation is not yet understood. The simplest explanations, either poor stirring or density variations, do not satisfy these observations: poor stirring would affect all of the peaks and density fluctuations would have greater effect on the lower energy peaks. Examination of the structure of monoclinic TNT shows that neither the (224) nor (112) planes appear to be important in defining the monoclinic structure (for example, planes of molecules do not lie along these Miller planes). Because we cannot define what is causing this phenomenon from the known experimental or structural considerations, we suggest it may be a hydrodynamic effect that does seem to be worthy of further study. The second factor is that mentioned previously in that low levels of solid material are not detectable in solution, limiting a full analysis of the evolving diffraction patterns. Despite the failure of a strict kinetics analysis we remain convinced that the general trends of the data and the observed changes point to the growth being dominated by a solvent-mediated phase transformation.

Conclusions

We conclude that the previously observed dependence of the nature of the polymorphic form of TNT on the solvent from which it is precipitated is not due to any stereospecific direction induced by solvent−solute interactions. The process reflects simply the initial precipitation of the metastable orthorhombic form followed by its conversion to the monoclinic form as expected on the basis of Ostwald's Rule of Stages. Because the initial solutions are saturated with respect to the monoclinic phase, the generation of a supersaturation (and thus implementation of Ostwald's law of stages) by addition of water is crucial. Its relatively poor solubility in the resulting mixed solvent effectively "isolates" the metastable form of TNT for a short period of time and slows down what would otherwise be a rapid solvent-mediated phase transformation. The generation of one form or the other is dependent on the balance of the rates of precipitation and of conversion coupled with the speed of isolation of the metastable product following its formation. A principal factor in the isolation of the metastable form is its solubility in the chosen solvent. However, the results of the cooling experiments show that it is necessary to disrupt the transport properties within the solution, otherwise little of any metastable phase will be obtained. Consideration of these factors should lead to the development of reliable procedures for the isolation of useful metastable polymorphic forms of a wide range of other chemical species of polymorphs which are similarly related.

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