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2,4,5-TRIPICRYL-S-TRIAZINE, TPT; IT'S CRYSTALLIZATION AND CRYSTAL DENSITY DETERMINATIONS

Naval Surface Weapons Center
Silver Spring, Maryland

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WHITE OAK LABORATORY

2,4,6-TRIPICRYL-s-TRIAZINE, TPT; IT'S CRYSTALLIZATION AND CRYSTAL DENSITY DETERMINATION

BY
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8 MARCH 1976

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) 2,4,6-Tripicryl-s-triazine, TPT, is normally crystallized from acetone-methanol solutions as an acetone solvate. The solvent of crystallization may be removed by heating, leaving a non-crystalline or pseudo crystalline solid, the density of which is not the true crystal density. Previous efforts to prepare crystalline TPT have not been successful. In this work, TPT was crystallized from a variety of solvents. In most cases,		

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solvates were formed; however, crystallization from *m*-dichlorobenzene produced crystals that were non-solvates, and were large enough for crystal density determinations. The density of these crystals was found to be 1.724 g/cc.

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2,4,6-TRIPICRYL-s-TRIAZINE, TPT; IT'S CRYSTALLIZATION AND CRYSTAL DENSITY DETERMINATION

This report describes a study of the crystallization of 2,4,6-tripicryl-s-triazine, TPT, a heat-resistant explosive. For the first time, true, non-solvated crystals have been prepared. The density of these crystals is 1.724 g/cc. The work reported here was performed under Task IR-144 and Task NSWC-0841/NASA.

Julius W. Enig
JULIUS W. ENIG
By direction

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2,4,6-TRIPICRYL-*s*-TRIAZINE, TPT; IT'S CRYSTALLIZATION AND CRYSTAL DENSITY DETERMINATION

I. INTRODUCTION

The heat-resistant explosive 2,4,6-tripicryl-*s*-triazine, TPT, shows considerable promise for use in hardware such as mild detonating cord (MDC) and flexible linear shaped charges (FLSC) at temperatures of 300°C and above. This explosive compound is readily synthesized from cyanuric chloride and picryl halides using the Ullmann biaryl synthesis (1), however its crystallization has presented problems. Although the compound can be readily crystallized from acetone or acetone-methanol solutions, the resulting crystals are 1:1 solvates with acetone. On heating at temperatures of 140°C, or higher, the bright yellow crystals loose their solvent of crystallization, becoming opaque and white, but retain essentially the same shape and size. When the process is observed on a hot stage and the heating is rapid, vigorous vibrations in the bed of crystals can be observed. The density of these pseudocrystals was previously found to be 1.67 g/cc (1).

The crystal density of an explosive is an important factor in determining its detonation properties. This can be illustrated by the comparison of the detonation pressures of RDX and HMX. On the basis of molecular structure and composition, it might be expected that these two compounds would have the same energetics. This is not the case. For example, the detonation pressures of RDX and HMX are 342 kbar and 382 kbar respectively, the difference being attributed to the difference in their crystal densities, 1.80 g/cc for RDX and 1.90 g/cc for HMX.

Since the desolvated pseudocrystals of TPT probably contain voids, their experimentally determined density was believed to be less than that of a true crystal, its theoretical maximum density (TMD). In order to determine the TMD, it was necessary to make true, unsolvated crystals of the compound. This was a feat which

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(1) J. C. Dacons and Michael E. Sitzmann, "Heat Resistant Explosives XXVI. The Synthesis and Properties of 2,4,6-Tripicryl-*s*-Triazine, TPT," NOLTR 68-64, 29 May 1968.

had not previously been accomplished, although most of the common laboratory solvents had been tried.

It was assumed that the crystals formed were unusually stable donor-acceptor complexes rather than occlusion complexes in which solvent molecules were simply trapped within the spaces of the TPT crystal lattice. Although this assumption was not necessarily a valid one, it did provide a base from which to start a search for a suitable solvent. The assumption was made primarily because acetone, and other solvents successfully used in the crystallization of TPT, seemed to be such excellent donors for TPT as an acceptor.

II. RESULTS AND DISCUSSION

One of the first solvents tried in this effort, was m-dinitrobenzene, a very poor donor, and the crystallization was done at temperatures near 200°C (see experimental section). The product was composed of agglomerates of small transparent prisms. When heated on a hot stage under the microscope, these crystals melted at 349-351°C without any obvious physical change prior to melting. It was therefore concluded that these were crystals of essentially pure TPT. However the agglomerates did not lend themselves well to crystal density determinations, and when broken up, the particles were too small.

Because of their structures, it was believed that the m-dihalobenzenes might also yield unsolvated crystals. Moreover, more conventional crystallization procedures could be used. The first of these solvents tried was m-dichlorobenzene. Samples of desolvated TPT from acetone-methanol were dissolved in boiling m-dichlorobenzene and the solutions were allowed to cool slowly. The products were small glistening colorless prisms. On heating below the melting point, these crystals showed no sign of change. When m-difluoro- and m-dibromobenzene were tried the products were very fine colorless needles and fine pale yellow prisms, respectively. On heating, both products gave questionable results and these solvents were not considered further.

In an effort to grow larger crystals from m-dichlorobenzene, the procedure of Taylor and Oesterling (2) was tried. The crystals were appreciably larger than those from the procedure described above, and were then subjected to mass spectral and gas chromatographic analyses. The former showed a trace of chlorine, and the latter showed the presence of m-dichlorobenzene in the amount of 0.01%. A 1:1 solvate requires 17.4% of this solvent. In addition

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(2) Francis Taylor, Jr. and R. E. Oesterling, "Heat Resistant Explosives XX. Production of Grade II HNS", NOLTR 65-142, 26 August 1965.

to the solvents discussed above, twenty-three others were tried without success. These are listed in tabular form below.

1. Acetic Acid
2. Acetic Anhydride
3. Acetonitrile
4. Benzonitrile
5. m-Bromoanisole
6. Bromobenzene
7. m-Bromotoluene
8. Chlorobenzene
9. Cyclohehanone
10. p-Difluorobenzene
11. N,N-Dimethyl Formamide
12. Epichlorohydrin
13. Ethylene Glycol Monobutyl Ether
14. Methyl Benzoate
15. Mesitylene
16. Nitric Acid (90%)
17. Nitrobenzene
18. Nitromethane
19. M-Nitrotoluene
20. 1,2,4-Trifluorobenzene
21. Xylene (mixed)
22. Dimethylsulfoxide/Sulfuric Acid
23. Dimethylsulfoxide/Water

All of the above solvents gave crystals that underwent obvious physical changes on heating below the melting point. In all cases the crystals lost their shiny surfaces and became opaque. The distinctly colored crystals lost their color, and some vibrated vigorously during the change. These changes were considered evidence that desolvation was taking place and no further consideration was given to these solvents.

Crystal density determinations according to the procedure of J. M. Rosen (3) are best carried out using a single large crystal; several smaller crystals can be used if they are of sufficient size to permit their positions in the bouyant lead perchlorate solutions to be accurately followed. Such was the case with the TPT crystals from m-dichlorobenzene using the procedure of Taylor and Oesterling. In six determinations the values varied over the range 1.721 - 1.726 g/cc for an average of 1.724 g/cc. Using the same procedure, the crystal density of the acetone solvate, after drying under vacuum at room temperature, was 1.637 g/cc. After desolvation by heating over night at 150°C under vacuum, the density of the pseudo crystal was found to be 1.666 g/cc. The previously reported value for the latter is 1.67 g/cc (1).

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(3) J. M. Rosen, "Micro Determination of the Crystal Density of Organic Compounds", NOLM 10656, 4 January 1950.

It is of interest to note that the density of the desolvated pseudo crystal is greater than that of the solvate itself. This indicates that although the solid after desolvation tends to retain the original shape of the crystal, there is considerable shrinkage which tends to fill the voids left by the solvent.

As pointed out above, the solvated products were assumed to be unusually stable charge transfer complexes; however, the validity of this assumption has not been established. Proof of the true nature of the solvates must await further study.

III. ACKNOWLEDGEMENTS

The author wishes to thank J. C. Hoffsommer and D. A. Kubose for mass spectral and gas chromatographic analyses, and J. M. Holden and C. W. Dickinson of this Center for helpful discussions on the nature of the TPT crystals.

IV. EXPERIMENTAL

Except in cases specificly described below, samples of desolvated TPT from acetone-methanol were dissolved in the various solvents by heating, then allowed to cool slowly. The crystals were recovered by suction filtration and dried on the funnel. In cases where inorganic acids and dimethylsulfoxide were used, the samples were washed with water prior to drying.

Crystallization from m-Dinitrobenzene. Approximately 2.5g of m-dinitrobenzene and 0.4g of TPT were mixed in a glass boat and placed inside the drying chamber of an Abderhalden drying apparatus over nitrobenzene. The pressure inside the drying chamber was very slowly reduced, using a vacuum pump, so as not to cause spattering. The m-dinitrobenzene slowly sublimed over into the cold zone of the apparatus leaving the TPT in the hot zone. Near the end, the pressure was reduced to a minimum and held for several hours. The procedure produced crystalline agglomerates not well suited for crystal density determinations. When broken up, the particles were too small. The melting point was 349-351°C (d).

Crystallization from m-Dichlorobenzene. Initially, TPT was recrystallized from m-dichlorobenzene using the general procedure described above. The procedure of Taylor and Oesterling (2), briefly described here, gave larger crystals which were more suitable for density measurements. The equipment consisted of a reflux apparatus equipped with a heated extraction chamber fitted with a sintered glass disc through which the refluxing solvent returned to the boiling flask. The TPT to be recrystallized was placed in the extraction chamber on the sintered glass disc and was slowly transferred to the boiling flask by the refluxing solvent. The process was enhanced by fitting the extraction chamber with a mechanical stirrer which was operated very slowly. The volume of the boiling flask was 200 ml, and 6.0g of TPT and 75 ml of m-dichlorobenzene were used. As the concentration of TPT in the boiling solvent increased, crystallization began. When all of the TPT had been removed from the extraction chamber, the crystals were removed by filtration while hot, washed with m-dichlorobenzene and dried at ambient temperature under vacuum. The melting point was 352-3°C, and there was no visible physical change below the melting point. Additional crystals which precipitated from the filtrate on cooling were smaller and were not used for density determination.

Crystal Density Determination. Three stock aqueous solutions of lead perchlorate having densities of 2.213, 1.701 and 1.400 g/cc were on hand. The procedure involved suspending a few crystals of the sample in approximately 3.5 ml of the lead perchlorate solution having a density of 1.701 g/cc in a 120 x 15 mm test tube, shaking to get random dispersion, then centrifuging at 4000-5000 rpm for two minutes. If the crystals moved to the top or settled to the bottom, then a small portion of the appropriate stock solution of lower or higher density was added and the suspension was again shaken and centrifuged. The process was repeated until the crystals remained randomly dispersed on centrifuging, indicating that the densities were matched. A sample of the solution was then transferred to a calibrated pycnometer and weighed. The weight of the solution divided by the weight of an equal volume of distilled water gives the density of the test solution which is the same as the density of the crystals. Using this procedure, the crystal densities of samples of TPT from m-dichlorobenzene and acetone-methanol were obtained along with the density of a desolvated sample of TPT from acetone-methanol. The results were as follows:

From m-Dichlorobenzene. Six determinations: 1.723, 1.726, 1.722, 1.726, 1.721, 1.725; avge. 1.724 g/cc

From Acetone-Methanol. Three determinations: 1.638, 1.641, 1.631; avge. 1.637 g/cc

Desolvated Crystals from Acetone-Methanol. Three determinations: 1.671, 1.662, 1.665; avge. 1.666 g/cc.