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THERMAL AND STABILITY STUDY OF TETRACENE USING DIFFERENTIAL SCANNING CALORIMETRY

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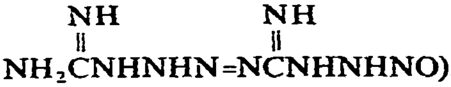
ABSTRACT

A thermal analysis study was made of tetracene using differential scanning calorimetry (DSC). The effect of different scan speeds was investigated. At scan speeds of 0.625 to 10°C min^{-1} two large rounded exothermic peaks were produced. The peaks occurred at an increasingly high temperature as the scan speed increased (for example, the peaks occurred at 128 and 130°C at a scan speed of 0.625°C min^{-1} and at 148 and 150°C at a scan speed of 10°C min^{-1}). When tetracene was heated at a scan speed of 80°C min^{-1} only one large sharp exothermic peak was produced. It is believed that the two peaks obtained at scan speeds of 0.625 to 10°C min^{-1} represent decomposition of the tetracene in two successive stages, while the one peak obtained at 80°C min^{-1} represents an explosion. A stability test for tetracene is proposed that involves heating of the tetracene in aluminum pans from the DSC apparatus in ovens at 100, 75, and 60°C, removing the pans and samples at intervals of 30 min, 24 h, and 7 days, respectively, subjecting the samples to DSC at 1.25°C min^{-1}, and noting the time interval in the oven that produces a DSC curve that shows obliteration of the second peak. Two lots of tetracene made by different processes showed marked differences in stability characteristics.

INTRODUCTION

Tetracene is 1-(5′-tetrazolyl)-4-guanyltetrazene hydrate,

(in the older literature and most military handbooks it is characterized as 1-guanyl-4-nitrosoaminoguanyltetrazene or 4-guanyl-1-(nitrosoaminoguanyl)-1-tetrazene,  $NH_2\overset{NH}{\overset{\|}{C}}NHNHN{=}N\overset{NH}{\overset{\|}{C}}NHNHNO$). The substance is an important explosive that has widespread use in priming compositions for ammunition and explosive charges for rivets[1–3]. It is made by reacting sodium nitrite with either aminoguanidine bicarbonate, aminoguanidine sulfate, or aminoguanidine nitrate in a neutral solution or a solution slightly acidified with acetic acid[1–6].

There are few data on the thermal behavior of tetracene in the literature. Hofmann and Roth[4], who first synthesized the material, stated that it did not melt but exploded at 140°C. Patinkin et al.[5] likewise found that the material did not melt but exploded at 135°C, as determined by spreading the sample in a thin train along the Dennis bar apparatus (a device consisting of a copper bar with an electric heater at one end to produce a gradient along the bar[7]). The military specification for tetracene (MIL-T-46938A)[8] gives a melting point and explosion point requirement for tetracene of 128 to 132°C, as determined by heating about 0.5–1 mg sample at a rate of 1 °C per 3 min in the Vanderkamp apparatus (a device consisting essentially of a capillary tube, a small electric heater, an enclosed air space, and a magnifying glass[9]). This and other laboratories have frequently observed that tetracene when heated in Vanderkamp apparatus shows an apparent melting point that occurs about 0.5°C before the explosion point (both the apparent melting point and explosion point occur in the interval of 128 to 132°C).

Yoffe[10] studied the thermal decomposition of tetracene in a technique whereby a pellet containing about 2 mg of the material was heated several minutes in a vessel (total volume of apparatus was 35 ml) under a vacuum and the reaction followed by observing the pressure. He found the decomposition of tetracene to be a complex matter. When heated at 120°C there was only slight decomposition, as indicated by the slight increase in pressure. When heated at 135°C there was a rapid increase in pressure and an explosion in 3.5 min. When heated at 172°C the pressure increased very abruptly (indicating rapid decomposition) but there was no explosion. Yoffe stated that the absence of an explosion at 172°C could be due to the rapid volatilization of a decomposition product that acts as a catalyst for the explosion. Yoffe found no indication of a melting point before the explosion point. He established that the gas generated during decomposition and explosion was primarily nitrogen.

When subjected to the 75°C International Heat Test (10-g sample), tetracene lost 0.5% of its weight in 48 h; when subjected to the 100°C Heat Test (0.6-g sample), tetracene lost 23.2% of its weight in the first 48 h, 3.4% in the next 48 h, but it did not explode in 100 h (refs. 2 and 3).

As far as is known, no extensive thermal work has been performed on tetracene using sophisticated thermal techniques. The laboratory, therefore, undertook an investigation of the thermal behavior of tetracene using differential scanning calorimetry (DSC). At the same time, an investigation was undertaken on the development of a stability test for tetracene using DSC. It is known that tetracene, that is stored, sometimes becomes less effective as an explosive for reasons that are not clear.

EXPERIMENTAL

Apparatus and materials

The instrumentation used in this study was a Perkin-Elmer 1B differential scanning calorimeter. The instrument was run at the low range (1 to 4 mcal sec^{-1}) and it was calibrated for zero correction at the indium (156°C) and lead (327°C) melting points. The chart speed was 0.5 in. min^{-1}. The samples were sealed into aluminum pans (Perkin-Elmer Part No. 219-0041). The carrier gas was helium.

Two lots of tetracene made at Frankford Arsenal were tested. One lot (Lot A) was made by the aminoguanidine carbonate process[1-3], while the second lot (Lot B) was made by a modified aminoguanidine sulfate process[6]. Tetracene is customarily stored under water. For the experimental work in this report, the material was transferred to a Buchner funnel (containing a Whatman No. 40 filter paper), washed well with water, and dried in a sulfuric desiccator for 24 h.

Procedure

The two lots of tetracene were run by DSC at scan speeds of 0.625, 1.25, 2.5, 5, 10, and 80°C min^{-1}. The sample size used for the runs at 0.625, 1.25, and 2.5°C min^{-1} was about 3 mg, while the sample size used for the runs at 5, 10, and 80°C min^{-1} was about 1 mg. The smaller size sample was necessary at the higher scan speeds to keep the peaks on the chart paper.

The stability test for tetracene involved heating the samples in the aluminum pans from the DSC apparatus in ovens at 100, 75, and 60°C, removing the pans and samples at intervals of 30 min, 24 h, and 7 days, respectively, subjecting the samples to DSC at 1.25°C min^{-1}, and noting the time interval in the oven that produced a DSC curve that showed obliteration of the second peak.

RESULTS AND DISCUSSION

Typical peaks obtained on subjecting the two lots of tetracene to DSC at 0.625, 1.25, 2.5, 5, and 10°C min^{-1} are shown in Figs. 1 and 2. A summary of all the data obtained for the DSC runs for these four scan speeds is shown in Table 1 (all peak measurements were made at the maximum of the peaks). The following conclusions can be drawn from the data: (a) at scan speeds of 0.625 to 10°C min^{-1} tetracene shows two large peaks separated by about 2 to 4°C, (b) the two peaks occur at a higher temperature as the scan speed increases, (c) the peaks for Lot A tetracene occur at about 4 to 8°C higher than peaks for Lot B tetracene.

When tetracene was heated by DSC at 80°C min^{-1} only one peak was obtained as shown in Fig. 3. These peaks occurred at 175 and 168°C for Lots A and B, respectively.

It is believed that the two large rounded peaks obtained by DSC at 0.625 to 10°C min^{-1} represent two stages of decomposition (such rounded peaks are frequently characteristic of decomposition). Also, it is believed that the sharp peak obtained by DSC at 80°C min^{-1} represents an explosion.

Since the peaks obtained were exothermic, tetracene cannot have a true melting point. Yet, the fact remains that a definite apparent melting point occurs before the explosion point when the material is tested in the Vanderkamp apparatus. It is

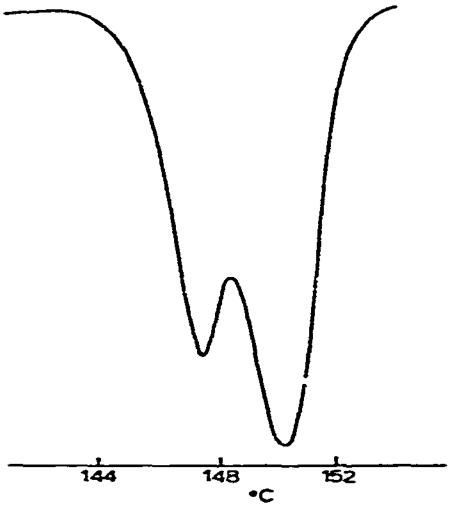


Fig. 1. DSC curve for tetracene at 1.25 °C min^{-1} (Lot B).

Fig. 2. DSC curve for tetracene at 10 °C min^{-1} (Lot A).

TABLE 1

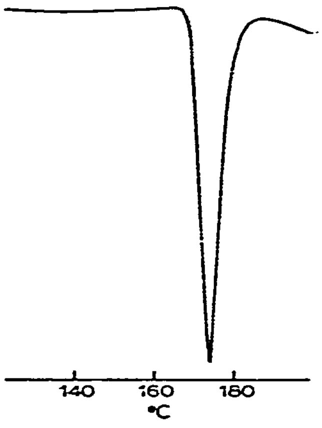
EFFECT OF SCAN SPEED ON DSC PEAKS OBTAINED FOR TWO LOTS OF TETRACENE (0.625 to 10 °C min^{-1})

Scan speed, (°C min^{-1})	*Location of peaks* (°C)			
	Lot A		*Lot B*	
	1st peak	*2nd peak*	*1st peak*	*2nd peak*
0.625	128	130	124	126.5
1.25	133.5	136	126	129
2.5	137.5	140	128.5	132.5
5	142	144.5	135	139
10	147.5	150	139.5	143.5

believed, therefore, that the first of the two peaks obtained at 0.625 to 10 °C min^{-1} represents the formation of a liquid decomposition product (and nitrogen).

It is difficult to correlate Yoffe's data[10] with the present investigation, since the manner of heating in the two studies is quite different. Yoffe's statement that there is a substance initially produced that triggers further decomposition catalytically would seem to be borne out by the closeness of the two peaks obtained at 0.625 to 10 °C min^{-1} by DSC.

Figs. 4 and 5 show the last two runs of the stability test at 100 °C for Lot A, while Figs. 6 and 7 show the last two runs of the stability test at 60 °C for Lot B. The time for deterioration was taken as the time in the oven that just caused obliteration of the second peak in the DSC run (Figs. 4 and 6). A summary of all the results



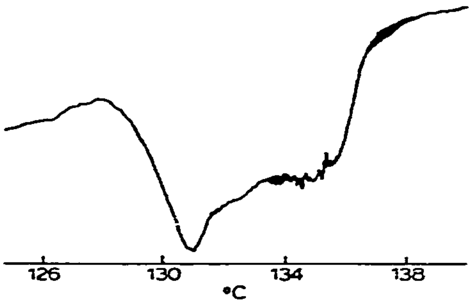
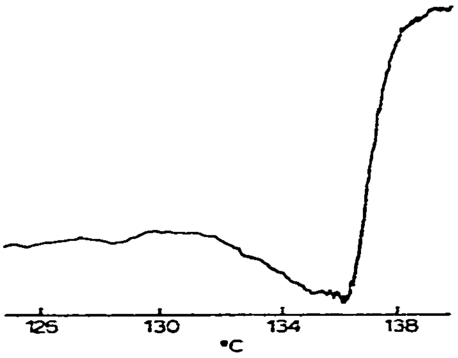


Fig. 3. DSC curve for tetracene at 80 °C min^{-1} (Lot A).

Fig. 4. Stability test for tetracene. DSC curve at 1.25 °C min^{-1} after storage at 100 °C for 7.5 h (Lot A).



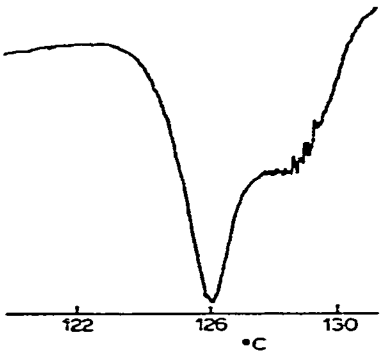


Fig. 5. Stability test for tetracene. DSC curve at 1.25 °C min^{-1} after storage at 100 °C for 8 h (Lot A).

Fig. 6. Stability test for tetracene. DSC curve at 1.25 °C min^{-1} after storage at 60 °C for 5 weeks (Lot A).

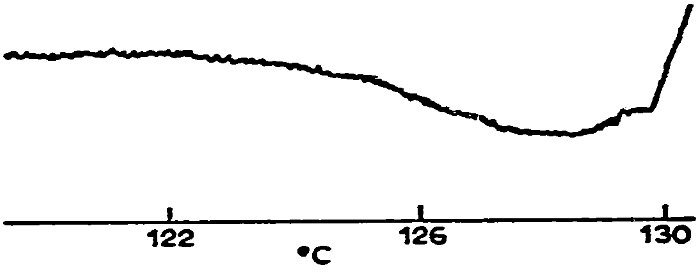


Fig. 7. Stability test for tetracene. DSC curve at 1.25 °C min^{-1} after storage at 60 °C for 6 weeks (Lot A).

obtained for the stability test is given in Table 2. It is seen that Lot A is much more stable than Lot B.

TABLE 2

SUMMARY OF DATA FOR STABILITY TEST FOR TETRACENE

Temp. of storage (°C)	*Time in oven that caused deterioration of tetracene as shown by DSC (1.25 °C min^{-1})*	
	Lot A	*Lot B*
100	7.5 h	3 h
75	14 days	8 days
60	>13 weeks	5 weeks

The authors have no explanation as to why tetracene that has deteriorated shows obliteration of the second peak. Obviously, however, the disappearance of the second peak would seem to be in keeping with the failure of tetracene to behave satisfactorily as an explosive, since the absence of the second peak shows less energy is available (the total energy is measured by the sum total of the areas under the exothermic peaks). If tetracene is heated for too long a time, both peaks disappear as was shown in Fig. 7.

The reason why Lot A tetracene is more stable than Lot B tetracene is uncertain. Chemical and physical examination of the two lots in accordance with MIL-T-46938A[8] showed no significant differences. The chemical and physical tests described in MIL-T-46938A are color and appearance (white to light yellow in color; needle-shaped crystals under a microscope), melting point and explosion point (128 to 132°C), granulation (100% through U.S. No. 45 sieve), specific gravity (1.60–1.70), heavy metals (none), nitrogen content (74.0–75.0%), sulfated ash (0.05% maximum, proposed). Examination of the two lots by infrared spectroscopy showed no detectable differences. It is quite possible that organic impurities, that cannot be detected by present analytical methods, are the cause of the great instability of Lot B. Tetracene cannot be purified by recrystallization, since the material is practically insoluble in useful solvents.

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