*Thermochimica Acta*, 80 (1984) 367–377
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# THERMAL STABILITY OF AN EXPLOSIVE DETONATOR

ALBERT S. TOMPA

*Naval Surface Weapons Center, White Oak, Silver Spring, MD (U.S.A.)*

(Received 24 May 1984)

## ABSTRACT

Mercuric 5-nitrotetrazole is a possible replacement for lead azide. The thermal decomposition peak maximum ranged from 185 to 270 °C as the heating rate increased from 0.1 to 100 °C $\text{min}^{-1}$. The activation energy and frequency factor for thermal decomposition were determined from dynamic and isothermal DSC and isothermal TG data; the average values were 38.8 kcal $\text{mol}^{-1}$ and $3.56 \times 10^{14}$ $\text{s}^{-1}$. A half-life experiment confirmed the kinetic constants and indicated that the decomposition reaction was first order. The heat of explosion was determined by a pressure DSC test and found to be 2587 J $\text{g}^{-1}$. The linear coefficient of expansion was $37 \pm 2 \times 10^{-6}$ °$\text{C}^{-1}$ from −60 to 160 °C and indicated secondary transitions near −10 and 90 °C. The specific heat was $0.0003154T + 0.1339$ in the region −40–90 °C. The critical temperature for a slab with a half-thickness of 0.035 cm was calculated to be 232 °C.

## INTRODUCTION

Mercuric 5-nitrotetrazole $[\text{Hg(NT)}_2]$ is a primary explosive detonant. It was developed as a less hazardous replacement for lead azide which upon hydrolysis is known to attack metals and form, in some cases, more sensitive materials. The explosive properties of $\text{Hg(NT)}_2$ have been studied by Scott [1] and found to be comparable to lead azide. Brown and Swallowe [2] studied the decomposition of $\text{Hg(NT)}_2$ by isothermal thermogravimetry (TG) and found activation energies of 160 kJ $\text{mol}^{-1}$ (38.2 kcal $\text{mol}^{-1}$) for the acceleratory period and 137 kJ $\text{mol}^{-1}$ (32.7 kcal $\text{mol}^{-1}$) for the deceleratory period by assuming values for the order of reaction of 2, 2.5, and 3.5; $\text{Hg(NT)}_2$ decomposed between 167 and 187 °C. Reddy and Chatterjee [3] carried out a thermal study by differential scanning calorimetry (DSC) and TG on mercury azotetrazole. They calculated activation energies for decomposition using several methods and found values ranging from 149 to 270 kJ $\text{mol}^{-1}$ (35–64 kcal $\text{mol}^{-1}$); exotherms were observed in the 144–160 °C region. In the present study the thermal stability of $\text{Hg(NT)}_2$ was investigated by isothermal and dynamic DSC and by isothermal TG. In addition, the specific heat, heat of explosion, half-life, and linear coefficient of expansion were determined by DSC and thermomechanical analysis (TMA).

## EXPERIMENTAL

### *Instrumentation*

A DuPont 1090 thermal analyzer was used with DSC, TG and TMA modules. All runs were carried out in a nitrogen atmosphere with a flow rate of 100 ml $\text{min}^{-1}$. DSC runs were carried out in a sealed pan with a pin-hole in the cover to permit decomposition gases to escape. A pressure DSC cell operating under 500 psi nitrogen was used for heat of explosion determinations.

### *Material*

$\text{Hg(NT)}_2$ was synthesized by Farncomb and Chang [4] in our laboratory using a procedure developed by Gilligan and Kamlet [5]. Purity analysis was 100 ± 1% based on UV atomic absorption, and dichromate titration methods developed by Glover [6].

### *Sample*

The mass of sample used was 0.8 ± 0.3 mg. A larger mass could be used at slower heating rates, i.e., 1.5 mg at 1 °C $\text{min}^{-1}$ and conversely a smaller mass had to be used at faster heating rates, i.e, 0.4 mg at 100 °C $\text{min}^{-1}$. A sample mass of approximately 1 mg and heating rates above 10 °C $\text{min}^{-1}$ resulted in the separation of the perforated sealed sample pan in DSC runs, and in the case of TG runs caused the counterweights to be blown off. For TMA runs the powdered $\text{Hg(NT)}_2$ was pressed at 15, 20, 30 and 50 kpsi into pellets that were 0.1 in. in height.

### *Procedure*

Dynamic DSC runs were carried out at twelve heating rates from 0.1 to 100 °C $\text{min}^{-1}$ and the corresponding peak maximum shifted from 185 to 270 °C, respectively. Isothermal DSC runs were at seventeen temperatures from 185 to 235 °C and the corresponding times to reach peak maximum were 120–3 min, respectively. Isothermal TG runs were at fifteen temperatures from 178 to 221 °C and the corresponding times to reach a fraction reaction of 0.8 were from 365 to 8 min, respectively. For both isothermal DSC and TG the modules were at the desired temperature before the sample was admitted. The TMA runs were conducted at 5 °C $\text{min}^{-1}$.

### *Kinetic methods*

Dynamic DSC data were analyzed according to the methods of Flynn and Wall [7] and Ozawa [8].

The basic equation is $\Delta \log \beta/\Delta(1/T) \approx 0.457E/R$, where $\beta$ is the programmed heating rate and $T$ is the temperature at the peak maximum (K). The Arrhenius frequency factor was calculated from (1) the equation $\log A = 0.457\ E/RT + 2.315 + \log \beta - \log E/R - \log F(C)$, where $F(C)$ is a function of the degree of conversion and (2) Rogers and Smith's [9] equation $\log A = \log \beta + \log E/RT_{\max}^2 + 0.435E/RT_{\max}$, where $T_{\max}$ is the reaction peak maximum. The isothermal DSC data were analyzed by the method of Rogers [10] for the rate, order, and activation energy from the decay/deceleratory part of the decomposition curve, and the induction time to reach the peak maximum using the method of Wall et al. [11] where $\log t/\Delta(1/T) = E/2.3R$ and $\log A = \log t + E/2.3RT$. The isothermal TG data were analyzed according to the method of Manche–Carroll [12], where $\log[\Delta\alpha/\Delta t/\Delta(1/T)]$ was plotted to obtain $E/2.3R$. The fraction reacted is $\alpha$ and $\Delta\alpha/\Delta t$ is the rate at fixed values of $\alpha$. The Arrhenius frequency factor was obtained from $\log A = E/2.3RT + \log(\Delta\alpha/\Delta t)$.

## DISCUSSION

### *Dynamic DSC*

Figure 1 shows dynamic DSC curves at three heating rates. Symmetric band shapes were observed at heating rates of 10 °C $\text{min}^{-1}$ and below. At 20 and 100 °C $\text{min}^{-1}$ the sealed sample pans with perforated covers containing 1-mg samples separated when the decomposition temperatures were reached. It appeared that the strong exothermic decomposition peak became an endothermic peak simply by increasing the heating rate. Obviously, this artifact may be explained by noting that the energy released in the perforated sealed pan was too great to be dissipated to the surroundings in the time interval it took to traverse the decomposition peak. An indication of this may be seen in the 20 °C $\text{min}^{-1}$ scan and by observing the baseline at

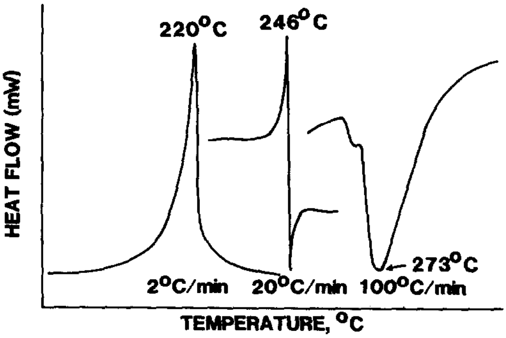


Fig. 1. DSC curves of $Hg(NT)_2$ at different heating rates in a perforated cell.

the start and end of the reaction. Symmetric exothermic band shapes were found at a heating rate of 100 °C $\text{min}^{-1}$ when the sample was in an open pan or in a perforated sealed pan run in an atmosphere of 500 psi nitrogen.

The variable heating rate data plotted in Fig. 2 gave an activation energy for thermal decomposition of 38.0 kcal $\text{mol}^{-1}$ and a frequency factor of $2.09 \times 10^{14}$ $\text{s}^{-1}$. The rate of heat release at the decomposition temperatures is also plotted in Fig. 1; values of 0.29 cal $\text{g}^{-1}$ $\text{s}^{-1}$ at 185 °C and 76.4 cal $\text{g}^{-1}$ $\text{s}^{-1}$ at 246 °C were calculated. For comparison, the rate of heat release for trinitrotoluene is 0.01 cal $\text{g}^{-1}$ $\text{s}^{-1}$ at 245 °C [13].

### *Heat of explosion*

This value was determined in a pressure DSC cell operating under 500 psi nitrogen to exclude the presence of air and combustion. The sample mass was accurately weighed (~ 1 mg) and the heating rate was 2 °C $\text{min}^{-1}$. The cell was previously calibrated with indium and zinc to obtain the cell constant at the decomposition temperature. The heat of explosion was 2587 J $\text{g}^{-1}$ ±50 for three determinations.

### *Isothermal DSC*

A typical isothermal DSC curve is shown in Fig. 3. For the analysis of the decay/deceleratory part of the DSC curve, the peak maximum is the starting point and the time at this point is taken as zero. The rate of decomposition at any time is taken as the vertical displacement from the baseline to the decay portion of the DSC curve. As the decomposition reaction proceeds, the rate decreases; the rate constant is the slope of the log displacement versus time plot (Fig. 4). The order of the reaction may be obtained from the

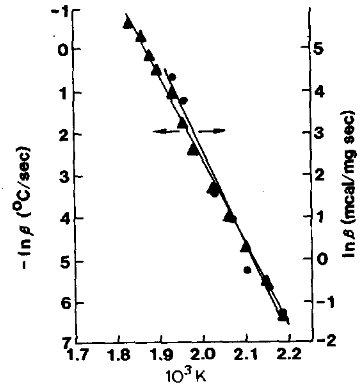


Fig. 2. DSC heating rate versus temperature plot. Left-hand side, $E = 38.0$ kcal $\text{mol}^{-1}$, $A = 2.09 \times 10^{14}$ $\text{s}^{-1}$; right-hand side, the rate of heat release at 184 and 246 °C is 0.29 and 76.4 cal $\text{g}^{-1}$ $\text{s}^{-1}$, respectively.

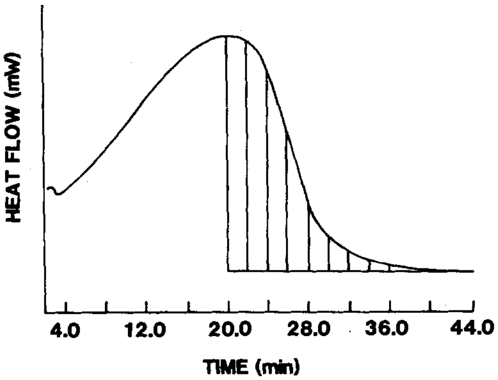
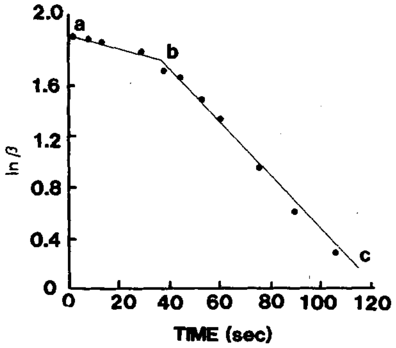


Fig. 3. Isothermal DSC curve of $Hg(NT)_2$ at 207 °C.



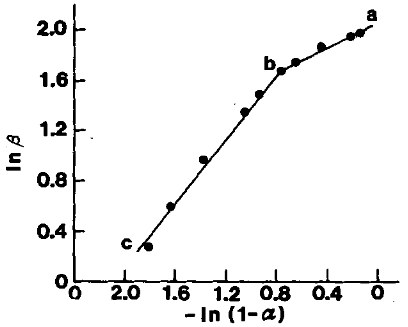
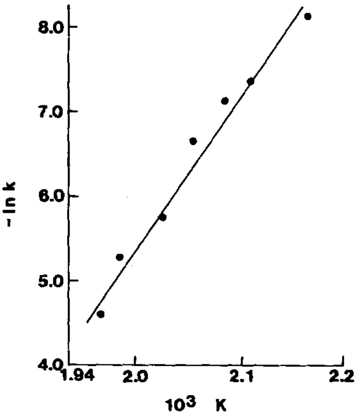


Fig. 4. Rate plot for $Hg(NT)_2$ from isothermal DSC data at 229 °C. a–b, $k = 5.1 \times 10^{-3}$ $s^{-1}$, b–c, $k = 2.3 \times 10^{-2}$ $s^{-1}$.

Fig. 5. Order plot for $Hg(NT)_2$ from isothermal DSC data at 229 °C. a–b, $n = 0.5$; b–c, $n = 1.2$; 12.3, 53.2 and 83.6% decomposition at a, b and c, respectively.



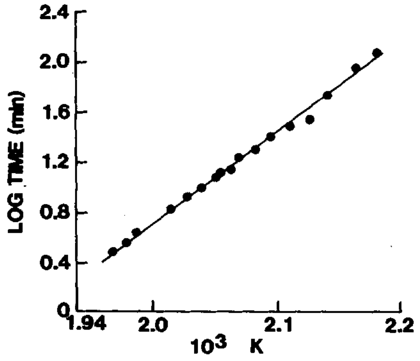


Fig. 6. Arrhenius plot of isothermal DSC decomposition data for $Hg(NT)_2$. $E = 35.8$ kcal $mol^{-1}$.

Fig. 7. Isothermal DSC data for time to reach peak maximum. $E = 33.8$ kcal $mol^{-1}$, $A = 1.89 \times 10^{12}$ $s^{-1}$.

slope of a plot of log vertical displacement (rate of reaction) versus the reactant fraction remaining (area fraction of the decay curve) at the end of each time interval as shown in Fig. 5. During the initial stages of decomposition the order of reaction is 0.3–0.5. After about 50% of the sample reacts the order becomes 1 as shown by the change in slope (Fig. 5). An Arrhenius plot using isothermal DSC data of ln $k/\Delta(1/T)$ is presented in Fig. 6; an activation energy of 35.8 kcal $mol^{-1}$ was found. Figure 7 shows an induction reaction time plot to reach the peak maximum of the decomposition curve. An activation energy of 33.8 kcal $mol^{-1}$ and a frequency factor of $1.89 \times 10^{12}$ $s^{-1}$ were calculated.

### *Thermogravimetry*

A typical TG curve at a slow heating rate is shown in Fig. 8. The inflection temperature is at 226 °C, which is in good agreement with the peak decomposition temperature of 220 °C given in the DSC curve in Fig. 1. There is a rapid weight loss over a few degrees in the dynamic TG run which

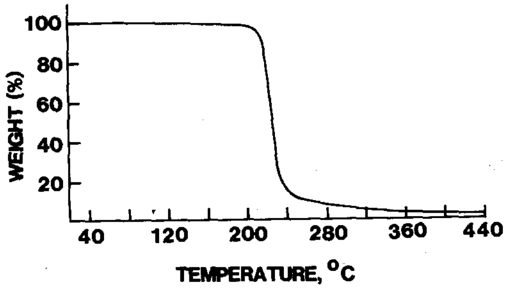
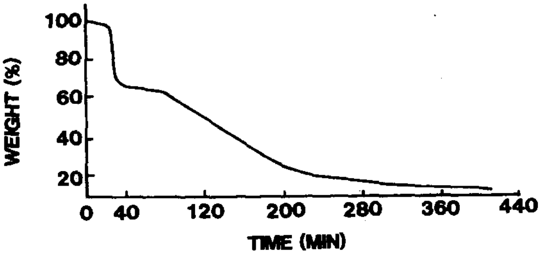


Fig. 8. TG curve of $Hg(NT)_2$ at 2 °C $min^{-1}$ in nitrogen.



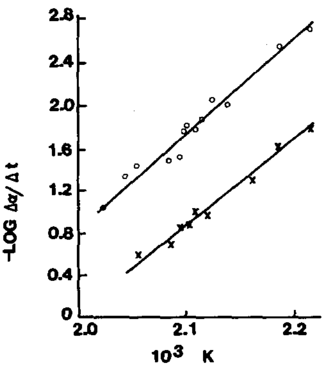


Fig. 9. Isothermal TG curve of $Hg(NT)_2$ at 184 °C in nitrogen.

Fig. 10. Arrhenius plot of isothermal TG decomposition data for $Hg(NT)_2$. (○) $\alpha$ values from 0.5 to 0.8, $E = 39.6$ kcal $mol^{-1}$, $A = 503 \times 10^{14}$ $s^{-1}$; (×) $\alpha$ values from 0.1 to 0.3, $E = 34.8$ kcal $mol^{-1}$, $A = 2.10 \times 10^{13}$ $s^{-1}$.

becomes even more pronounced at higher heating rates, therefore, limiting its usefulness in obtaining kinetic data. The isothermal TG curve in Fig. 9 showed a rather sharp break after about a 32% weight loss followed by a long gradual weight loss. The tetrazole moiety is 31.7% of $Hg(NT)_2$. Kinetic data were obtained for both regions using the Manche–Carroll method [12] (Fig. 10).

### *Activation energies*

Table 1 lists the activation energies and frequency factors obtained for the thermal decomposition of $Hg(NT)_2$. There is very good agreement between dynamic DSC and isothermal TG data and their values were averaged for subsequent use in half-life and critical temperature calculations. Slightly lower values (~ 10%) were found by isothermal DSC from induction/delay time and from decay curve measurements. These values were also in good agreement with that obtained from the first break in the isothermal TG curves. The kinetic constants found in this study agreed with those reported by Brown and Swallowe [2].

### *Half-life for thermal decomposition*

The method proposed by Duswalt [14] for an isothermal half-life test to check the validity of activation energy and frequency factor values obtained from kinetic data was followed. The average values for activation energy and frequency factor were taken as 38.8 kcal $mol^{-1}$ and $3.56 \times 10^{14}$ $s^{-1}$ (Table 1). The half-life equation for first-order decay is $t_{1/2} = 0.693/k$; if $t_{1/2}$ is taken as 60 min then $k = 0.01155$ $min^{-1}$. Substitution into $\log k = \log A - E/2.3RT$ and solving for temperature gives 192°C. The sample was aged in the pressure DSC cell at 192°C for 60 min, cooled to room temperature and run at 2°C $min^{-1}$ in the same manner as the heat of explosion experiment. The enthalpy for decomposition was 1340 J $g^{-1}$; the zero time value was 2587 J $g^{-1}$. Therefore, 1340/2587 = 51.8%; theoretical value is 50%. Thus,

TABLE 1

Kinetic constants for thermal decomposition of $Hg(NT)_2$

| Method | $E$ (kcal $mol^{-1}$) | $A$ ($s^{-1}$) |
|---|---|---|
| Dynamic DSC | 38,0 | $2.09 \times 10^{14}$ |
| Isothermal TG ($\alpha = 0.5$–$0.8$) | 39.6 | $5.03 \times 10^{14}$ |
| Average value | 38.8 | $3.53 \times 10^{14}$ |
| Isothermal DSC (induction) | 33.8 | $1.89 \times 10^{12}$ |
| Isothermal DSC (decay curve) | 35.8 | |
| Isothermal TG ($\alpha = 0.1$–$0.3$) | 34.9 | $2.10 \times 10^{13}$ |

TABLE 2

Half-life of $Hg(NT)_2$ at various temperatures

| Temp. (K) | Half-life |
|---|---|
| 300 | $1.2 \times 10^6$ years |
| 400 | 37 days |
| 500 | 3 min |
| 600 | 0.3 s |
| 1000 | $6 \times 10^{-7}$ s |

there is excellent agreement between the found and theoretical values and, consequently, one can have confidence in the kinetic values found in this study. The decomposition reaction is first order which is in agreement with the value obtained from the order plot using isothermal DSC data and Rogers [10] method.

The half-life of $Hg(NT)_2$ at various temperatures may be calculated using the equations described earlier. Table 2 shows changes in half-life from millions of years to a millionth of a second as the temperature is tripled. At 500 K the calculated half-life is 3 min which is in good agreement with the isothermal DSC induction time of 4.5 min to reach the decomposition peak maximum.

*Critical temperature*

The critical temperature of an energetic material may be calculated using the Frank-Kamenetskii [15] equation

$$T_c = E/R \ln\left(\frac{\rho a^2 Q A E}{\lambda R T_c^2 \delta}\right)$$

where: $T_c$ = critical temperature; $R$ = gas constant; $a$ = radius of a sphere or cylinder, or the half-thickness of a slab; $\rho$ = density; $Q$ = heat of reaction for the self-heating process; $A$ = Arrhenius frequency factor; $E$ = activation energy; $\lambda$ = thermal conductivity; $\delta$ = shape factor, 0.88 for infinite slabs, 2.00 for infinite cylinders, and 3.32 for spheres. Rogers [16] has shown that there is good agreement between the calculated and experimental values of $T_c$ for many common explosive ingredients. Calculated values were based on a DSC determination of chemical parameters such as activation energy and frequency factor. The values used for $Hg(NT)_2$ were $R = 1.987$ cal $mol^{-1}$ $K^{-1}$, $\rho = 3.235$ g $cm^{-1}$, $a = 0.035$ cm, $\lambda = 9.3 \times 10^{-4}$ cal $s^{-1}$ $cm^{-1}$ $K^{-1}$, and $\delta = 0.88$. The calculated value for $T_c$ was 505 K (232°C).

*Specific heat*

The specific heat determination by DSC is straightforward and was carried out as shown in Fig. 11. Sapphire was used as the standard to calculate the cell constant because its specific heat is known over a wide range of temperature. Briefly, the thermal lags between the empty pans and the sample/reference were measured; sample mass was 20–30 mg, sapphire disk was 61 mg, and the heating rate was 20 °C min$^{-1}$. Usually, about ten DSC runs are made with the instrument parameters held constant. The specific heat may be calculated from (1) $C_s = C_r m_r Y_s M_s^{-1} Y_r^{-1}$, where the subscripts s and r refer to sample and reference and $C$, $m$, and $Y$ are the specific heat, mass, and vertical displacement from empty pans to sample/reference, respectively, at a given temperature, and (2) $C_s = 60EqY_sH^{-1}m_s^{-1}$, where $E$ is the cell constant, $q$ is the heat flow (mW cm$^{-1}$), and $H$ is the heating rate. Figure 12 shows the specific heat increasing with temperature from −40 to 90 °C and a smaller rate of increase from 90 to 160 °C. The equation for the specific heat rise from −40 to 90 °C is $C_p = 0.0003154T + 0.1339$, where $T$ is the temperature (°C). The precision of the data is ±0.003.

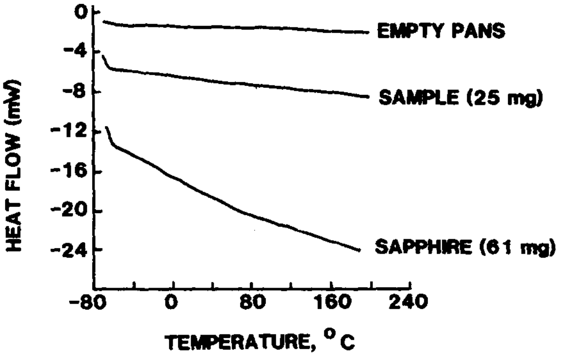


Fig. 11. DSC determination of the specific heat of $Hg(NT)_2$.

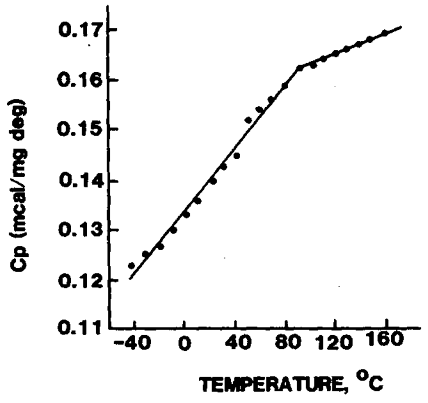


Fig. 12. Specific heat of $Hg(NT)_2$ as a function of temperature.

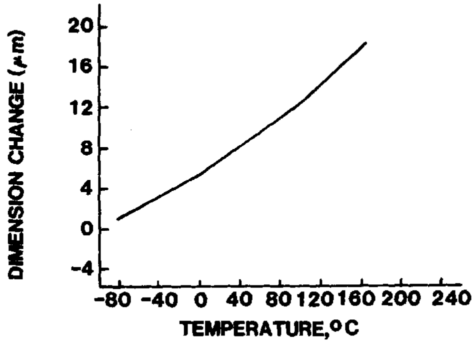


Fig. 13. TMA curve of an $Hg(NT)_2$ pellet.

### *Linear expansion*

The linear expansion behavior was followed from −80 to 160 °C (Fig. 13). There are small bends in the curve near −10 and 90 °C which indicate secondary transitions in these regions. Figure 12 showed an abrupt change in specific heat around 90 °C which is in agreement with changes observed in the expansion curve. Pellets of $Hg(NT)_2$ were pressed at pressures of 20 to 50 kpsi without any noticeable changes in expansion behavior. The linear coefficient of expansion ($\alpha$) was calculated from the equation $\alpha = C\Delta L\ \Delta T^{-1}\ L^{-1}$, where $\Delta L \Delta T^{-1}$ is the slope of the change in length ($\mu$m) with change in temperature (°C), $L$ is the original height of the sample in micrometers, and $C$ is the calibration constant found using aluminum and lead slugs as standards; it is the ratio of the actual to found values for the linear coefficient of expansion for the two standards. The value of $\alpha$ for $Hg(NT)_2$ was $37 \pm 2 \times 10^{-6}\,°C^{-1}$ from −60 to 160 °C.

## SUMMARY

The thermal stability and characterization data for $Hg(NT)_2$ are given in Table 3.

TABLE 3

Summary of thermal analysis data for $Hg(NT)_2$

(1) Thermal decomposition peak, 185 °C at heating rate of 0.1 °C $min^{-1}$ 270 °C at heating rate of 100 °C $min^{-1}$

(2) Rate of heat release, 0.29 cal $g^{-1}$ $s^{-1}$ at 185 °C, 76.4 cal $g^{-1}$ $s^{-1}$ at 246 °C

(3) Kinetic constants for thermal decomposition, $E = 38.8$ kcal $mol^{-1}$, $A = 3.56 \times 10^{14}$ $s^{-1}$

(4) Heat of explosion (atmosphere of 500 psi $N_2$), $\Delta H = 2587$ J $g^{-1}$

(5) Half-life (192 °C/60 min), $\Delta H = 1340$ J $g^{-1} = 51.87\%$ of theoretical

(6) Linear coefficient of expansion, $\alpha = 37 \pm 2 \times 10^{-6}\,°C^{-1}$ from −60 to 160 °C.
0.1-inch/2540-$\mu$m pellets pressed at 15–50 kpsi, secondary transitions near −10 and 90 °C

(7) Specific heat, $C_p = 0.0003154T + 0.1339$ from −40 to 90 °C

(8) Critical temperature for slab with half-thickness of 0.035 cm is 232 °C

## ACKNOWLEDGMENTS

The author thanks Mr. G.R. Laib and Mr. R.E. Farncomb for helpful discussions and the sample used in this study, and Mrs. R. Washington for technical assistance.

## REFERENCES

1 C. Scott, Proc. Int. Conf. Research in Primary Explosives, E.R.D.E., Vol. 2, 1975, Paper 15.
2 M.E. Brown and G.M. Swallowe, Thermochim. Acta, 49 (1981) 333.
3 G. Om Reddy and A.K. Chatterjee, Thermochim. Acta, 66 (1983) 231.
4 R.E. Farncomb and M.S. Chang, NSWC/WOL TR 77-82, 1976.
5 W.H. Gilligan and M.J. Kamlet, NSWC/WOL TR 76-146, 1976.
6 D.J. Glover, NSWC/WOL TR 77-71, 1977.
7 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand., Sect. A, 70 (1968) 478.
8 T. Ozawa, J. Therm. Anal., 2 (1970) 301.
9 R.N. Rogers and L.C. Smith, Anal. Chem., 39 (1967) 1024.
10 R.N. Rogers, Thermochim. Acta, 3 (1972) 437.
11 L.A. Wall, J.H. Flynn and S. Straus, Polym. Eng. Sci., 10 (1970) 19.
12 E.P. Manche and B. Carroll, Thermochim. Acta., 25 (1978) 77.
13 D.R. Stull, AIChE Monogr. Ser., 73 (1977) 96.
14 A.A. Duswalt, Thermochim. Acta, 8 (1974) 57.
15 D.A. Frank-Kamenetskii, Acta Physicochem., USSR, 10 (1939) 365.
16 R.N. Rogers, Thermochim. Acta, 11 (1975) 131.