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Coefficient of Thermal Expansion of Pentaerythritol Tetranitrate and Hexahydro-1,3,5-trinitro-s-triazine (RDX)

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Measurements have been made of the coefficients of thermal expansion as a function of temperature of single crystals of pentaerythritol tetranitrate (PETN) and hexahydro-1,3,5-trinitro-s-triazine (RDX). Two independent coefficients of linear expansion were measured for tetragonal PETN and three for orthorhombic RDX.

The thermal expansion coefficient is a second-order symmetric tensor and hence contains six independent constants for a triclinic crystal. This number is reduced for crystals with higher symmetry. Hexahydro-1,3,5-trinitro-s-triazine (RDX, $C_3H_6N_6O_6$) crystallizes with orthorhombic symmetry, and its thermal expansion is expressed by three coefficients of linear expansion measured along the principal crystallographic axes. Pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$) is tetragonal, and two coefficients, one along the unique crystallographic axis and one perpendicular to it, describe the thermal expansion. The direction of measurement of the coefficient of linear thermal expansion is indicated by a subscript giving the crystal face normal to the direction of measurement—e.g., $\alpha_{(120)}$ is measured in a direction perpendicular to the (120) crystal face. It happens, for these materials, that $\alpha_{(100)}$ is measured parallel to the a crystallographic axis, and similarly $\alpha_{(010)}$ and $\alpha_{(001)}$ parallel b and c, respectively.

This paper reports measurements of the coefficients of linear thermal expansion $[\alpha = (1/L)(dL/dT)]$ as a function of temperature for PETN from -160–$100°C$ and for RDX from -160–$140°C$. The coefficients of volume thermal expansion $[\beta = (1/V)(dV/dT)]$, as computed from the linear coefficients, are also reported.

EXPERIMENTAL

Materials. Baker Analyzed reagent-grade acetone and the chemically purest military grade PETN and RDX obtainable were used as starting materials. Nutrient stock crystals were made by recrystallization from filtered acetone solutions. Single crystals of PETN and RDX were then grown by standard cold-finger techniques from acetone solutions. The final crystals were not analyzed for chemical purity but are presumably purer than the 99 wt % purity of the starting materials. PETN and RDX are both powerful secondary explosives and should be treated with caution. The hazard of spontaneous exothermic heating to explosion and the large size of the crystals were factors determining the maximum temperatures at which expansion data were measured. The crystals were selected for measurement on the basis of optical perfection and well-developed planar faces and were rejected if they showed any evidence of nonparallel extinction with polarized light, visible distortion of an image reflected from a face, or other evidence of vicinal face development.

Apparatus. A DuPont Model 900 Thermal Analyzer equipped with a Model 941 Thermomechanical Analyzer (TMA) was used to determine linear thermal expansion. The 900 Thermal Analyzer is a solid-state electronic temperature programmer-controller which permits a wide range of temperature scanning conditions. One of several plug-in modules is the 941 TMA, which uses a movable-core differential transformer to detect vertical displacement of a sample surface as a function of temperature. The output of the transformer is specified to be linear within ±0.5% up to 0.05 in. of total displacement; however, our instrument was found to be linear to at least ±0.0625 in. from its null position. The output of the 941 module is amplified and plotted on the 900 recorder as a function of temperature on charts printed to provide direct reading of sample temperature. The maximum amplification factor for our 900 Thermal Analyzer converts a change of 0.0001232 in. of sample height to a change of 1 in. in ordinate on the chart paper.

The TMA as received from DuPont was found to be quite sensitive to changes in ambient temperature, and changes in laboratory temperature were sufficient to drive the recorder off scale when set to its maximum amplification. The amplitude of this signal was reduced to about 1 in. by moving the instrument to an air-conditioned laboratory with a constant average long-term temperature but with a short-term (15-min) temperature swing of 1°C. The Dewar cap, which is closely coupled to the differential transformer support and the top of the sample holder, was changed to provide it with constant-temperature circulating water, and the remainder of the differential-transformer support housing was isolated from rapid changes in room temperature by further insulation. These changes increased the warm-up time of the instrument to about 3 hr, but reduced the recorded ambient temperature signal to ±0.01 in.

The shape of the baseline indicated a heat leak between the sample heater and the differential transformer. Eight spaced aluminum-foil baffles were inserted inside the sample-holder tube near the Dewar cap to control radiant and convective

heat flow. Insulation was added outside the sample-holder tube to fill the space between the heater assembly and the Dewar cap. These changes decreased the displacement of the baseline by a factor of three for elevated sample temperatures and increased baseline reproducibility so that a correction factor could be determined. Baseline corrections were determined as functions of sample height, heating rate, and temperature from curves obtained on fused quartz samples for each of the temperature ranges of the graph paper of the TMA.

The amplification factors for the various scales of the 941 TMA-900 Thermal Analyzer combination were determined directly rather than in the indirect manner suggested in ref. 2. The amplification factor was determined at room temperature for the least sensitive scale with steel ball bearings which differed in diameter by 0.0625 in. The null position of the differential transformer is set with one ball in position. That ball is then replaced with the other, and the difference in chart reading is determined. Other scale-amplification factors were determined relative to this least sensitive scale by measuring the relative gains for the various scales with respect to the electronic zero point. These gains are determined by fixing the core of the differential transformer, displacing the transformer from its null position, taking chart readings for the various scales, displacing the transformer to the opposite side of the null position, remeasuring the deflections, and, finally, combining measurements so as to eliminate the slight difference between electronic zero and transformer null.

The temperature calibration of the TMA graph papers was checked by measuring, at an atmospheric pressure of 578 mm Hg, the boiling temperatures of nitrogen ($-200°C$) and water (90.7°C), the sublimation temperature of carbon dioxide ($-81.5°C$), and the melting points of water (0.1°C), benzoic acid (121°C), sodium nitrate (333°C), and potassium dichromate (401°C). The calibration temperatures for nitrogen and potassium dichromate both differ from their accepted values by 2°C or more, but these points are outside the region of interest. Coefficients of thermal expansion are insensitive to errors in absolute temperature, so that no effort was made to correct the reported coefficients for any systematic errors in indicated temperature.

Calculation of the coefficient of thermal expansion is accomplished in the following manner. The sample height (usually in the range of 0.12–0.4 in.) is determined at room temperature to an accuracy of ±0.0001 in. The sample is transferred to the sample holder, and the probe is applied to the sample with an overpressure of about 15 psi to ensure good contact. The sample is then cooled carefully to a temperature at least 20°C below the lowest temperature of interest. The sample temperature is raised at a uniform and slow (1–5°C/min) rate while the output of the differential transformer is recorded as a function of temperature. The ordinates of the curve on the chart paper are measured to ±0.0025 in. at temperature intervals of 10–25°C along the curve, and the curve is then represented by a cubical least-squares spline curve fit with knots spaced uniformly so as to include two data points on the average. A cubical spline function is a special subclass of piecewise polynominal functions of third degree that is joined smoothly at its knots so that it has two continuous derivatives—i.e., there is a discontinuity possible only in the third derivative at the knots. This type of function has four very desirable features in the present case, namely, it is flexible, it is linear in the parameters (easy to compute), convenient to use (ordinates and slopes are easily determined), and a systematic error in slopes obtained from the raw data can be minimized. The accuracy with which the spline curves represent the data is shown by the average variance (1.4 $\times$ 10^{-5} in. squared), average difference (0.0016 in.), and maximum difference (0.0134 in.) between the calculated and measured, on the chart paper, ordinates for the 27 fits or 653 data points of RDX and PETN.

Spline interpolation is used to calculate, at temperatures midway between adjacent data points, slopes, and ordinates,

which are then converted into dL/dT and L by correcting for scale amplification factor, baseline slope, and the thermal expansion of fused quartz (1). The coefficients of linear thermal expansion computed from these results are shown as data points in Figures 1 and 2. Results from several runs could be com-
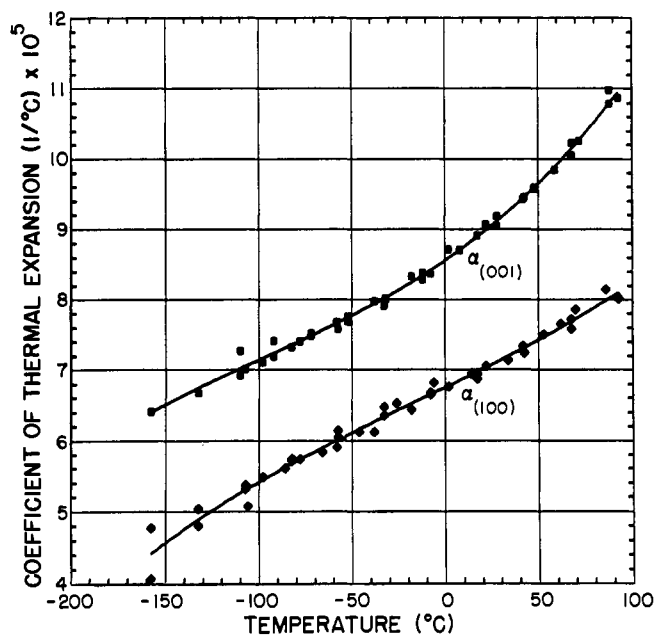

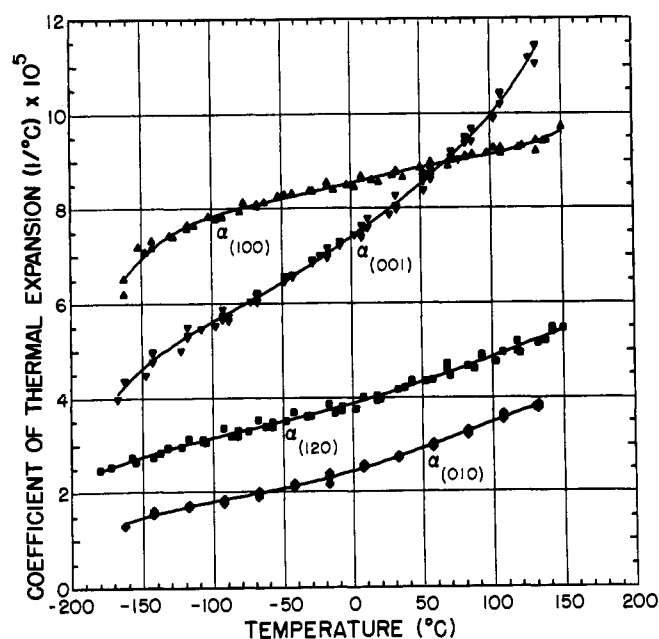Figure 1. Linear coefficients of PETN

Figure 2. Linear coefficients of RDX

Table I. Coefficient of Linear Thermal Expansion of Aluminum

Temp, °C	10^5 α Measured, °C^{-1}	10^5 α (1), °C^{-1}
-123	1.66	1.72
-73	2.00	2.00
-23	2.21	2.19
$27+$	2.33	2.32
$+77$	2.40	2.41
$+127$	2.47	2.49

Table II. Parameters for Thermal Expansion Least-Squares Curves

(Thermal expansion coefficient $= P_1 + P_2T + P_3T^2 + \ldots P_6T^5$. The parameter-estimated standard deviations are enclosed in parentheses and apply to the right-most digits. Unlisted parameters are statistically insignificant)

Coefficient	Temp range, °C	$P_1 \times 10^5$	$P_2 \times 10^7$	$P_3 \times 10^{10}$	$P_4 \times 10^{12}$	$P_5 \times 10^{15}$	$P_6 \times 10^{18}$	Variance of fit $\times 10^{13}$
PETN α(001)	−160–100	8.552(19)	1.821(35)	6.305(427)	2.175(402)			6.50
PETN α(100)	−160–100	6.749(30)	1.282(51)	0.738(644)	1.269(552)			14.85
PETN β (vol)	−160–100	22.050(47)	4.385(80)	7.78(101)	4.713(841)			
RDX α(100)	−160–150	8.531(16)	0.673(58)		−1.29(88)	−4.79(84)	1.01(30)	9.21
RDX α(001)	−160–135	7.391(24)	2.073(27)	3.17(71)		7.90(373)	1.02(12)	13.16
RDX α(120)	−180–150	3.876(20)	0.828(30)	1.55(45)	0.30(19)	−2.60(186)		7.39
RDX α(010) meas	−160–135	2.439(10)	0.842(7)	2.58(27)		−5.59(132)		1.91
RDX α(010) comb	−160–135	2.408	0.879	2.32		−3.74		
RDX β (vol)		18.33	3.625	5.48	−1.25	−0.63	2.03	

bined and fitted again by a spline function; however, spline fits can only be expressed in tabular form. A more concise form, when suitable, is the least-squares polynomial that is used for the final fitted curves.

The apparatus and data-reduction procedure were checked by determining the coefficient of linear thermal expansion of aluminum. The measured coefficient is compared with a literature value (1) in Table I.

RESULTS AND DISCUSSION

The single crystals of PETN used in this study exhibited well-formed (100) faces but no (001) faces, so that it was necessary to cut the crystals in order to measure $\alpha_{(001)}$. The experimental results and derived least-squares curves for $\alpha_{(100)}$ and $\alpha_{(001)}$ are illustrated in Figure 1. A first-degree approximation for the coefficient of volume thermal expansion (β) for PETN is $2\alpha_{(100)} + \alpha_{(001)}$. The parameters for the least-squares curves are given in Table II.

The calculated linear coefficient for a randomly oriented multicrystal pressing of PETN is one third of the volume coefficient and ranges from $7.65 \times 10^{-5}/°C$ at 20°C to $8.99 \times 10^{-5}/°C$ at 90°C. Roth and Blackburn (5) have measured such a linear coefficient as $11.3 \pm 0.8 \times 10^{-5}/°C$ between room temperature and 110°C, a value significantly higher than ours.

RDX crystallizes in the orthorhombic system; it will, therefore, have three principal coefficients of linear thermal expansion, corresponding to expansion along the three crystallographic axes. The axis orientation chosen for this study is such that the unit-cell dimensions are $a = 11.61$, $b = 13.18$, and $c = 10.72$Å, an orientation used by McCrone (4) in his article on the crystallographic data of RDX. The crystals suitable for measurement had well-developed (120) and (111) faces, neither being particularly desirable. Several crystals had (100) or (001) faces, but only two acceptable crystals with (010) faces were obtained. The experimental results and derived least-squares fitted curves for $\alpha_{(100)}$, $\alpha_{(010)}$ measured, $\alpha_{(001)}$, and $\alpha_{(120)}$ are shown in Figure 2. The parameters for

the least-squares curves are given in Table II. The linear coefficient, $\alpha_{(010)}$, can be calculated from $\alpha_{(120)}$, $\alpha_{(100)}$, and the temperature-corrected unit-cell dimensions from the equation $\alpha_{(120)} = [4a^2\alpha_{(010)} + b^2\alpha_{(100)}]/(4a^2 + b^2)$. The parameters for a curve, $\alpha_{(010)}$ combined—that is, the average of $\alpha_{(010)}$ calculated and $\alpha_{(010)}$ measured—are listed in Table II. The coefficient of volume expansion is essentially the sum of $\alpha_{(100)}$, $\alpha_{(010)}$, and $\alpha_{(001)}$, and its parameters are also listed. Filhol (3) has measured the coefficients of thermal expansion of RDX from changes in the unit-cell parameters as determined by X-ray diffraction. He reports $\alpha_{(100)} = 5.99 \times 10^{-5}/°C$, $\alpha_{(010)} = 1.74 \times 10^{-5}/°C$ and $\alpha_{(001)} = 5.43 \times 10^{-5}/°C$ from −158–175°C. These values are significantly lower than those reported here, and there is no obvious explanation for the discrepancy.

ACKNOWLEDGMENT

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Correction

In the paper, "Improved Equation for Prediction of Saturated Liquid Density," by Calvin F. Spencer and Ronald P. Danner [J. Chem. Eng. Data, 17, 236 (1972)], Equation 2 should read:

$$\frac{1}{\rho_s} = \left[\frac{RT_c}{P_c}\right] Z_{RA}^{[1+(1-T_r)^{2/7}]} \qquad (2)$$