AUG 07 1985

CONF-850736--49

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

LA-UR--85-2310

DE85 015685

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TETRANITRATE SINGLE CRYSTALS

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SUBMITTED TO The Fourth APS Topical Conference on Shock Waves in Condensed Matter

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POP PLOT AND ARRHENIUS PARAMETERS FOR <110> PENTAERYTHRITOL TETRANITRATE
SINGLE CRYSTALS

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ABSTRACT

Plane shock initiation sensitivity measurements for <110> single crystal pentaerythritol tetranitrate were extended to 20 GPa. The data of run distance versus input stress do not fall on the usual straight line on the Pop plot. From these data Arrhenius parameters were calculated. Computed activation energy was 6.4 kcal/mole, and the frequency factor was 5×10^6 /s. These are much lower than values obtained from isothermal heating experiments. These results can be used to support the idea that the uniaxial strain due to the shock leads to heterogeneous heating of the homogeneous material.

Explosives have traditionally been separated into two types: Homogeneous and heterogeneous. Homogeneous explosives include liquids and single crystals. Heterogeneous explosives include powder compacts, mixtures and slurries; hot spots are important in these materials. Initiation of detonation and detonation failure are believed to proceed by different mechanisms in homogeneous and heterogeneous explosives. Initiation of detonation in homogeneous explosives is believed to proceed by thermal explosion at the rear boundary, and detonation failure proceeds by transverse failure waves.

Data on plane shock initiation of <110> single crystal pentaerythritol tetranitrate (PETN) are presented here. The plane shock wave was generated by a 203-mm diameter explosive plane-wave lens, a pad of booster explosive, and a polymethylmethacrylate attenuator plate. Shock trajectories in the wedge samples were recorded with a rotating mirror camera. Hugoniot points and time and distance to detonation were obtained from the records. Shock sensitivity has been measured to 20 GPa. The data represent by far the largest range of input stresses used on a homogeneous explosive. The data in the Pop plot (Fig. 1) are not fitted by the usual straight line, unlike heterogeneous explosives. Since no other homogeneous explosive has been studied over such a large range of input stresses, it is hard to say if it is unique among homogeneous explosives.

Figure 1. Pop plot for <110> PETN single crystals.

Hardesty did an extensive study of liquid nitromethane.¹ He found Arrhenius parameters obtained from induction time measurements for the thermal explosion in shock experiments to be much smaller than the gas phase constants (Table 1). It seemed worthwhile to extract Arrhenius parameters from the PETN wedge data in the usual way,^{2,3,4} using

$$t_i = v^{-1} \frac{T_o^2}{T_F T_A} \exp(T_A/T_o) ,$$

where v is the frequency factor, T_F is the temperature rise through the reaction zone, T_o is shock temperature, and T_A is activation temperature. Induction time t_i was extracted from the wedge data as

$$t_i = \left(1 - \frac{U-u}{D} \right) t^* ,$$

where t^* is time to detonation at the shock front, D is detonation velocity at the precompressed density, and U and u are shock and particle velocities respectively. The energy parameter calculated is the Gibbs free energy of activation. One is assuming that the same activation energy is operative at all densities and temperatures sampled. An Arrhenius plot is shown in Fig. 2. A nonlinear least squares fitting program was used to obtain

parameters from the thermal explosion equation. An activation energy of 6.4 kcal/mole and a frequency factor of 5×10^6 /s were found. In comparison, the results from isothermal heating experiments on liquid PETN are 47 kcal/mole and 6×10^{19} /s.⁶ This is a much larger difference than that found for nitromethane (Table 1). The discrepancy will be discussed in later paragraphs.

Table 1. Arrhenius Parameters

Material	Shock		Isothermal	
	Activation Energy	Frequency Factor	Activation Energy	Frequency Factor
	(kcal/mole)	(s ⁻¹)	(kcal/mole)	(s ⁻¹)
PETN(a)	6.4	5×10^6	47	6×10^{19}
Nitromethane(b)	23.	3×10^9	53	4×10^{15}

- (a) Shock data is for <110> crystals; isothermal data is for liquid phase (Ref. 6).
 (b) Shock data from Ref. 1; Isothermal data is for gas phase (Ref. 7).

One notes that the straight line fit to PETN data in Fig. 2 yields nonrandom residuals, perhaps implying that the decomposition is not unimolecular. It could also mean that there are different regimes of behavior at low and high stresses. It should be noted that Lee and coworkers showed that static high pressure suppresses the thermal decomposition of PETN.⁸ It is also true that the assumption of the thermal explosion model that the ratio of the activation energy to the shock thermal energy is much greater than one, is not well satisfied for the PETN value computed here.

Calculated shock temperatures for PETN are shown in Fig. 3. The Hugoniot of single crystal PETN was taken as $U = 2.74 + 1.81u$, density as 1.779 g/cm^3 , heat capacity as 1000 J/kg-K , and the Grüneisen constant as 1.15. Note the position of the melt temperature relative to the shock temperatures. The melt phase line is not known, but in drop-hammer impact

Figure 3. Bulk shock temperature for PETN.

tests at Cambridge it is found that PETN melts before ignition occurs.⁹ This could also be the case in uniaxial shock compression.

Another aspect of PETN must be addressed. It has been shown that shock sensitivity depends on crystal orientation.¹⁰ This suggests that plasticity plays a role in initiation of detonation. Adiabatic shear bands have been observed in PETN during high strain rate deformation.¹¹ This means that the temperature distribution is probably not homogeneous in shocked PETN. The initial decomposition may be taking place in hot shear bands. If ignition occurs in shear bands we can say that the Arrhenius parameters we calculated using the bulk temperature are low for that reason and in serious error; the initial decomposition is taking place at temperatures much higher than the bulk temperature. One may summarize by observing that the explosive PETN is a homogeneous, anisotropic material subject to plastic instability in uniaxial strain.

These results affect our picture of what we call homogeneous explosives. Even in a liquid there will be shear flow in uniaxial shock compression. Whether instability of the viscous flow occurs and leads to inhomogeneous heating is not known, but it is something to consider.

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