Predicting the Detonation Velocity of CHNO Explosives by a Simple Method

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Abstract

A simplified method is shown, based on a semi-empirical procedure, to estimate the detonation velocities of CHNO explosives at various loading densities. It is assumed that the product composition consists almost of CO, CO₂, H₂O and N₂ for oxygen-rich explosives. In addition solid carbon and H₂ are also counted for an oxygen-lean explosive. The approximate detonation temperature, as a second needed parameter, can be calculated from the total heat capacity of the detonation products and the heat of formation of the explosive by PM3 procedure. The detonation velocities of some well-known CHNO explosives, calculated by the simple procedure, fit well with measured detonation velocities and the results from the well-established BKW-EOS computer code.

Keywords: Detonation Products, Detonation Velocity, Heat of Formation, PM3 Method

1 Introduction

Two indicators for the performance of explosives are: Detonation velocity and pressure. A simple explanation of detonation is given by Chapman and Jouguet based on the assumption that the chemical reaction takes place at the moment when the shock compresses the material [1]. The Chapman-Jouguet (C-J) detonation velocity of an explosive is the velocity at which the chemical reaction traverses the explosive, assuming there is no energy loss at the boundary of the material. In fact, observed detonation velocities can be extrapolated to this ideal C-J value without difficulty. The C-J detonation velocity serves as an accurately obtained measure of performance. The C-J velocity and pressure can be determined from experiments but the detonation temperature and composition of the products are almost unknown. The application of hydrodynamic theory for determining the detonation properties usually requires an equation of state for the detonation products. Kamlet and coworkers [6–9] introduced empirical equations for the calculation of the detonation velocity and pressure of CHNO explosives at loading densities greater than 1.0 g/cm³. To calculate the C-J detonation velocity and pressure usually requires the experimental solid state heat of formation as well as the (initial) loading density and the molecular formula of an explosive.

For many years detonation velocity and pressure have been considered as the principal measure of performance of detonating explosives. A continuing need exists in the field of energetic materials for reliable prediction of detonation velocity and energy delivery. The purpose of this work is to present a new method for predicting the detonation velocity of CHNO explosives, by assuming a reliable decomposition reaction, from the heat of formation of explosive in gas phase calculated by semi-empirical PM3 method [10] and heat capacities of detonation products at any loading density. PM3 is a second re-parameterization of MNDO, functionally similar to AM1, but with some significant improvements [11]. An important criterion for this work in opposite of previous work is that there is no need to know the measured solid or liquid heat of formation or any experimental data of CHNO explosives.

2 Characteristics of Detonation Velocity Performance of CHNO Explosives

One of the fundamental goals within the field of an energetic material has been to predict various properties related to performance before expanding resources in its synthesis. Elimination of any poor candidate of a new explosive due to performance problems at an early state of the development is highly desirable for a chemist.
The energy content of an explosive can be determined by the heat of formation or by the heat of detonation. An estimate of the heat of detonation can be obtained from the heat of decomposition of the explosive that is the difference between the heat of formation of the explosive and the detonation products per gram of explosive [6]. The GIPF methodology and quantum mechanical calculations of an explosive molecule can be used to evaluate the heat of detonation [12].

As a first step in our attempt to express the detonation velocity as a function of certain calculated parameters, we have explored the factors that can influence the detonation velocity. It can be inferred that a high detonation velocity, the same as detonation pressure [13], is promoted by light gaseous detonation products and a high positive heat of formation per unit weight of explosive.

The determination of detonation products can be made through thermochemical equilibrium calculations, experimental measurement or by identifying an appropriate decomposition reaction. Depending upon the composition of CHNO explosives, the typical detonation products of high explosives are CO, CO₂, H₂O, N₂ and solid carbon as well as minor amounts of H₂, NH₂, O₂, N₂, NO and other chemical species [14]. For explosives with zero or positive oxygen balance, the detonation products do not involve solid carbon. The detonation products are obtained at high pressure and temperature simultaneously. Examination of detonation products for CHNO explosives predicted by the Cheetah 2.0/JCZS calculations indicate that more than 94% of the gaseous species consist of only H₂O, H₂, N₂, CO₂ and CO [15]. Kamlet and Jacobs assumed that for CHNO explosives, the detonation products compose of only four compounds H₂O, N₂, CO₂ and solid carbon (but not CO and H₂) [6]. Since CO is one of the major detonation products, we can imagine a more reliable decomposition procedure so that the decomposition products consist of H₂O, H₂, N₂, CO₂, CO, O₂ (for explosive with excess of oxygen, e.g. NG) and solid carbon. We have explored the use of one of these techniques, with all nitrogen assumed to go to N₂ and for oxygen rich explosives, e.g. PETN and RDX, with oxygen preferentially forming H₂O and or CO and CO₂ in that order. For an oxygen-lean explosive, e.g. TNT, solid carbon instead of CO₂ are also counted as major products.

The heat of detonation as a quantity used to assess a candidate’s detonation performance is the energy available to do mechanical work. The approximate heat of detonation per mole can be determined from heats of formation of reactants and products of detonation through:

\[ \Delta_{app} H = \Delta_f H(\text{detonation products}) - \Delta_f H(\text{explosive}) \]  \hspace{1cm} (1)

The equilibrium composition of the product gases must be determined in order to evaluate the heat of the detonation.

The performance of an explosive strongly depends on producing high temperature in a very short time. The approximate heat of detonation per mole can be related to the approximation of the detonation temperature, \( T_{app} \), by assuming that \( \Delta_{app} H \) is used entirely to heat the product gases to \( T_{app} \), so that

\[ T_{app} = \frac{298.15K \cdot \sum C_{pi} - \Delta_{app} H}{\sum C_{pi}} \]  \hspace{1cm} (2)

where \( C_{pi} \) is the heat capacity of the \( i \)-th component of the detonation products which can be obtained from JANAF thermochemical data [16] at or near the approximate detonation temperature. Equations (1) and (2) show that a large positive heat of formation of the explosive favors a high \( T_{app} \). In Equation (2) it is assumed that \( \Delta_{app} H \) is constant over the temperature range between 298.15 K and \( T_{app} \). In order to simplify the method for obtaining the approximate detonation temperature, we have decided to use the estimated gas phase heat of formation of the explosive calculated by PM3 procedure instead of the experimental heat of formation. This condition excludes the crystal effects of explosive and in this situation there is no need to know the experimental heat of formation which is an important input data for usual thermochemical computer code.

One important property of an energetic material is its density. This value, along with the experimental heat of formation, will then be used to estimate the detonation properties from a thermochemical code, e.g. BKW-EOS, or Kamlet’s method. Experiments show that a linear relationship exists between C-J detonation velocity and loading density. They also reveal that C-J detonation pressure is roughly proportional to cubic of loading density.

The final step is to investigate the relation between C-J detonation velocity, \( T_{app} \), the number of gaseous products based on the above decomposition procedure, and the loading density. The decomposition products and other necessary parameters are given in Table 1. By plotting the C-J detonation velocity at a given loading density versus various combinations of the number of moles of gaseous products per unit weight of explosive and \( T_{app} \) of various CHNO explosives which cover a wide range of explosives in oxygen balance, the following linear relationship, as shown in Figure 1, is obtained:

\[ \text{Table 1. Parameters used in calculations.} \]

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Reaction Products</th>
<th>( T_{app} (K) )</th>
<th>( \eta^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>CO + 2N₂ + H₂O + H₂</td>
<td>2716</td>
<td>0.0481</td>
</tr>
<tr>
<td>HNAB</td>
<td>12CO + 4N₂ + 2H₂</td>
<td>2824</td>
<td>0.0398</td>
</tr>
<tr>
<td>PA</td>
<td>6CO + 1.5N₂ + H₂O + 0.5H₂</td>
<td>2469</td>
<td>0.0393</td>
</tr>
<tr>
<td>DATB</td>
<td>6CO + 2.5N₂ + 2H₂</td>
<td>1962</td>
<td>0.0453</td>
</tr>
<tr>
<td>TETRYL</td>
<td>7CO + 2.5N₂ + 1.5H₂ + H₂O</td>
<td>3126</td>
<td>0.0418</td>
</tr>
<tr>
<td>TNT</td>
<td>C(s) + 6CO + 1.5N₂ + 2.5H₂</td>
<td>2122</td>
<td>0.0441</td>
</tr>
<tr>
<td>NG</td>
<td>3CO₂ + 1.5N₂ + 2.5H₂O + 0.25O₂</td>
<td>4254</td>
<td>0.0319</td>
</tr>
<tr>
<td>NM</td>
<td>CO + 0.5N₂ + 0.5H₂ + H₂O</td>
<td>2553</td>
<td>0.0492</td>
</tr>
<tr>
<td>PETN</td>
<td>3CO₂ + 2CO + 2N₂ + 4H₂O</td>
<td>3808</td>
<td>0.0348</td>
</tr>
<tr>
<td>RDX</td>
<td>3CO + 3N₂ + 3H₂O</td>
<td>3750</td>
<td>0.0405</td>
</tr>
</tbody>
</table>

\[^a\text{See glossary of compound names and chemical formulas.}\]
\[^a\text{Number of gaseous products available per unit weight of explosive.}\]
\[ V_{CJ} = 0.314(\eta T_{app})^{1/2} \rho_0 + 1.95 \]

where \( V_{CJ} \) is the C-J detonation velocity, \( \rho_0 \) is the loading density and \( \eta \) is the number of moles of gaseous products per unit weight of explosive. As indicated in Table 2, good agreement is obtained between measured and calculated detonation velocities at defined experimental initial explosive density.

3 Comparison of the Method with the BKW-EOS Computer Code

The prediction of the detonation velocity for pure CHNO explosives using the thermochemical code BKW-EOS corresponded well to the experimental values. Two sets of parameters were used by the BKW-EOS to fit experiments carried out with CHNO explosives [3]. The first set fits the C-J state of explosive with nearly oxygen balance (RDX), the second set of parameters is recommended for low oxygen balance (TNT). The BKW-EOS, in spite of the weak theoretical basis, still plays an important role in predicting detonation properties of high explosives as compared to the other thermochemical computer codes [14]. As shown in Table 2, excellent agreement is obtained between the measured values of detonation velocity and the calculated values by the new method and also with respect to the complicated BKW-EOS code for any loading density of pure CHNO explosives.

4 Conclusion

Measurements of detonation velocity are probably good within a few percent meanwhile detonation pressure measurements are good within about 20% [17]. Since the detonation reactions are complicated phenomena with high detonation reaction rates, we can use some simple approximation to calculate the detonation velocity. We have assumed a reliable approach in predicting the decomposition properties of high explosives as compared to the other thermochemical computer codes [14]. As shown in Table 2, excellent agreement is obtained between the measured values of detonation velocity and the calculated values by the new method and also with respect to the complicated BKW-EOS code for any loading density of pure CHNO explosives.

Table 2. Comparison between the calculated \( V_{CJ} \) by the correlation and BKW-EOS computer code [17] with measured values.

<table>
<thead>
<tr>
<th>Explosive</th>
<th>( \rho_0 ) (g/cm(^3))</th>
<th>C-J Detonation Velocity (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATB</td>
<td>1.788</td>
<td>7.25; 7.96; 7.52</td>
</tr>
<tr>
<td>TETRYL</td>
<td>1.70</td>
<td>8.05; 7.63; 7.56</td>
</tr>
<tr>
<td>HNAB</td>
<td>1.60</td>
<td>7.28; 7.16; 7.31</td>
</tr>
<tr>
<td>NG</td>
<td>1.59</td>
<td>7.77; 7.70; 7.65</td>
</tr>
<tr>
<td>NM</td>
<td>1.13</td>
<td>5.93; 6.48; 6.35</td>
</tr>
<tr>
<td>PETN</td>
<td>0.25</td>
<td>2.85; 3.41; 2.83(^b)</td>
</tr>
<tr>
<td>RDX</td>
<td>0.56</td>
<td>4.12; 4.77; 4.05(^c)</td>
</tr>
<tr>
<td>DATB</td>
<td>0.70</td>
<td>4.66; 5.24; 4.65(^c)</td>
</tr>
<tr>
<td>PETN</td>
<td>0.95</td>
<td>5.63; 5.99; 5.80(^b)</td>
</tr>
<tr>
<td>NM</td>
<td>1.10</td>
<td>6.21; 6.41; 6.18(^b)</td>
</tr>
<tr>
<td>PETN</td>
<td>1.29</td>
<td>6.94; 6.97; 7.00(^f)</td>
</tr>
<tr>
<td>NM</td>
<td>1.46</td>
<td>7.60; 7.51; 7.60(^f)</td>
</tr>
<tr>
<td>PETN</td>
<td>1.60</td>
<td>8.14; 7.99; 8.25</td>
</tr>
<tr>
<td>TNT(^d)</td>
<td>1.70</td>
<td>8.80; 8.64; 8.70</td>
</tr>
<tr>
<td>PA</td>
<td>1.60</td>
<td>9.32; 9.70; 9.32</td>
</tr>
<tr>
<td>NQ</td>
<td>1.629</td>
<td>7.80; 8.07; 7.98(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Measured values of detonation pressure taken from Dobratz and Crawford [18] except were noted.
\(^b\) Mader [17]
\(^c\) Horning et al. [19]
\(^d\) TNT parameter

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velocity of CHNO explosives at any loading density of interest.

5 References


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Glossary of Compound Names

DATB 1,3-Diamino-2,4,6-trinitrobenzene (C₆H₅N₅O₆)
HNAB Bis(2,4,6-trinitrophenyl)-diazine (C₁₂H₄N₈O₁₂)
NG Nitroglycerine (C₃H₅N₃O₉)
NM Nitromethane (CH₃NO₂)
NQ Nitroguanidine (CH₄N₄O₂)
PA Picric acid (C₆H₅N₃O₃)
PETN Pentaerythritol tetranitramine (C₅H₈N₄O₁₂)
RDX Cyclomethylene trinitramine (C₃H₆N₆O₆)
TETRYL N-methyl-N-nitro-2,4,6-trinitroaniline (C₇H₅N₅O₈)
TNT 2,4,6-Trinitrotoluene (C₇H₅N₃O₆)

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