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, CO_2, H_2O and N_2 for oxygen-rich explosives. In addition solid carbon and H_2 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. The detonation performance of condensed explosives can no longer be treated by the ideal gas equation of state. Some of the widely used empirical and semi-empirical methods are based on the development of equations of state, required to describe shock and detonation performance of condensed explosives.

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A computer code, e.g. TIGER computer code [2], describing the detonation on the basis of the solution of Euler's hydrodynamic equation, requires an equation of state. Some of the well-known equations of state, as representative examples, include: the Becker-Kistiakowsky-Wilson equation of state (BKW-EOS) [3], the Jacobs-Cowperthwaite-Zwisler equation of state (JCZ-EOS) [4], Kihara-Hikita-Tanaka (KHT-EOS) [5]. Although the JCZ-EOS calculations have a strong theoretical basis, the BKW-EOS is the most widely used method for the prediction of detonation properties. 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, CO_2, H_2O, N_2 and solid carbon as well as minor amounts of H_2, NH_3, O_2, N_2, 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 H_2O, H_2, N_2, CO_2 and CO [15]. Kamlet and Jacobs assumed that for CHNO explosives, the detonation products compose of only four compounds H_2O, N_2, CO_2 and solid carbon (but not CO and H_2) [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 H_2O, H_2, N_2, CO_2, CO, O_2 (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 N_2 and for oxygen rich explosives, e.g. PETN and RDX, with oxygen preferentially forming H_2O and or CO and CO_2 in that order. For an oxygen-lean explosive, e.g. TNT, solid carbon and H_2 instead of CO_2 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:

$$\Delta_{app}H = \Delta_f H(\text{detonation products}) - \Delta_f H(\text{explosive}) \quad (1)$$

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

$$T_{app} = \frac{298.15\text{K} \cdot \sum_i C_{P,i} - \Delta_{app}H}{\sum_i C_{P,i}} \quad (2)$$

where $C_{p,i}$ 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:

Table 1. Parameters used in calculations.

Explosive[a]	Reaction Products	T_{app}(K)	η[b]
NQ	$CO + 2N_2 + H_2O + H_2$	2716	0.0481
HNAB	$12CO + 4N_2 + 2H_2$	2824	0.0398
PA	$6CO + 1.5N_2 + H_2O + 0.5H_2$	2469	0.0393
DATB	$6CO + 2.5N_2 + 2.5H_2$	1962	0.0453
TETRYL	$7CO + 2.5N_2 + 1.5H_2 + H_2O$	3126	0.0418
TNT	$C(s) + 6CO + 1.5N_2 + 2.5H_2$	2122	0.0441
NG	$3CO_2 + 1.5N_2 + 2.5H_2O + 0.25O_2$	4254	0.0319
NM	$CO + 0.5N_2 + 0.5H_2 + H_2O$	2553	0.0492
PETN	$3CO_2 + 2CO + 2N_2 + 4H_2O$	3808	0.0348
RDX	$3CO + 3N_2 + 3H_2O$	3750	0.0405

[a] See glossary of compound names and chemical formulas
[b] Number of gaseous products available per unit weight of explosive
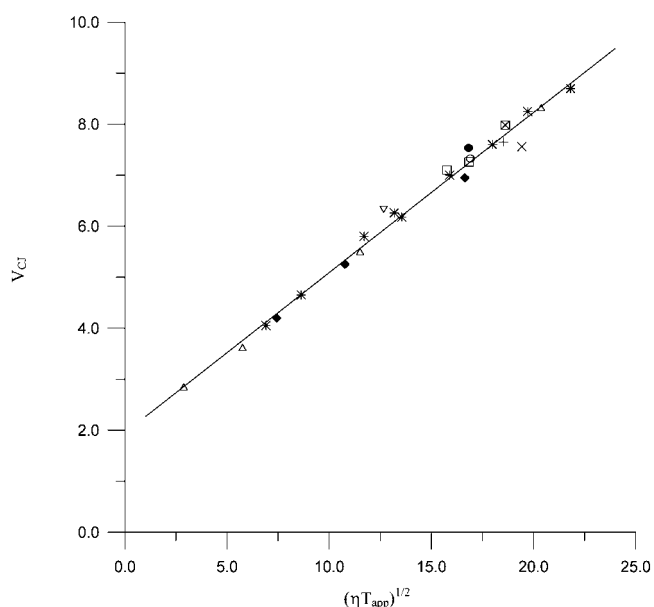
Figure 1. The experimental C-J Detonation velocity versus $(\eta T_{app})^{1/2}\rho_0$, where heat of formation calculated by PM3 procedure is used to estimate the approximate detonation temperature. The points are: + NG; × TETRYL; ◆ TNT; ● DATB; △ PETN; * RDX; ▽ NM; ● HNAB; □ PA; ⊠ NQ.

$$V_{CJ} = 0.314(\eta T_{app})^{1/2}\rho_0 + 1.95 \qquad (3)$$

where V_{CJ} is the C-J detonation velocity, ρ_0 is the loading density and η is the number of moles of gaseous products per unit weigh 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.

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

Explosive	ρ_0 (g/cm³)	C-J Detonation Velocity (km/s)		
		New Method	BKW-EOS	Experiment[a]
DATB	1.788	7.25	7.96	7.52
TETRYL	1.70	8.05	7.63	7.56
HNAB	1.60	7.28	7.16	7.31
NG	1.59	7.77	7.70	7.65
NM	1.13	5.93	6.48	6.35
PETN	0.25	2.85	3.41	2.83[b]
	0.50	3.76	4.31	3.60[b]
	1.00	5.56	5.95	5.48[b]
	1.77	8.35	8.42	8.30b
RDX	0.56	4.12	4.77	4.05[c]
	0.70	4.66	5.24	4.65[c]
	0.95	5.63	5.99	5.80[c]
	1.10	6.21	6.41	6.18[c]
	1.29	6.94	6.97	7.00[c]
	1.46	7.60	7.51	7.60[c]
	1.60	8.14	7.99	8.25
	1.70	8.80	8.64	8.70
TNT[d]	0.732	4.28	4.51	4.20[b]
	1.061	5.33	5.34	5.25[b]
	1.64	7.17	6.95	6.95b
PA	1.60	6.90	7.03	7.10
	1.71	7.24	7.40	7.26
NQ	1.629	7.80	8.07	7.98[b]

[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

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 products of CHNO explosives for both oxygen-lean and -rich compounds, where H_2O, H_2, N_2, CO_2, CO and solid carbon are major products. The effect of the explosive's energy content on the performance, as a second parameter in determining the detonation velocity, can be expressed via approximate detonation temperature. Calculated heat of formation of the explosive by PM3 procedure and heat capacities of detonation products are the parameters that can be used to obtain T_{app}. Although the complicated thermochemical computer codes usually have a stronger theoretical basis for the prediction of detonation properties than the method proposed here, those calculations also require experimental heat of formation as input. The methodology presented here has the advantage that the heat of formation does not need to be measured for calculating the detonation velocity of CHNO explosives at specified initial density. As shown in Table 2, a simple theoretical approach can help us to estimate the detonation

velocity of CHNO explosives at any loading density of interest.

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Glossary of Compound Names

DATB	1,3-Diamino-2,4,6-trinitrobenzene ($C_6H_5N_5O_6$)
HNAB	Bis(2,4,6-trinitrophenyl)-diazine ($C_{12}H_4N_8O_{12}$)
NG	Nitroglycerine ($C_3H_5N_3O_9$)
NM	Nitromethane (CH_3NO_2)
NQ	Nitroguanidine ($CH_4N_4O_2$)
PA	Picric acid ($C_6H_3N_3O_7$)
PETN	Pentaerythritol tetranitramine ($C_5H_8N_4O_{12}$)
RDX	Cyclomethylene trinitramine ($C_3H_6N_6O_6$)
TETRYL	N-methyl-N-nitro-2,4,6-trinitroaniline ($C_7H_5N_5O_8$)
TNT	2,4,6-Trinitrotoluene ($C_7H_5N_3O_6$)