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Prediction of densities of acyclic and cyclic nitramines, nitrate esters and nitroaliphatic compounds for evaluation of their detonation performance

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Abstract

A novel approach to density prediction by elemental composition is developed for various important classes of explosives. Some correlations based on two different models are introduced for 82 different energetic compounds whose molecules contain functional groups common to $C_aH_bN_cO_d$ explosives. These include acyclic and cyclic nitramines, nitrate esters and nitroaliphatic compounds. Of the 69 well-known and recently new synthesized organic explosives for which direct comparison could be made with Tarver group additivity method, root mean square (rms) of deviation for 19 acyclic and cyclic nitramines is 2.839 and 3.412 while for 50 nitrate esters and nitroaliphatic explosives is 1.936 and 1.752 for new and Tarver's method, respectively. This method is the simplest procedure for calculating density of energetic compounds which gives good results as compared to well-developed group additivity method for estimation density of organic explosives.

Keywords: Crystal density; Correlation; Nitramines; Nitrate esters; Nitroaliphatics; Elemental composition

1. Introduction

It is determined that the energy which a detonation wave releases within and behind itself will depend upon the mass of explosive traversed per unit area of the wave. However, detonation velocity appears to be proportional to loading density. Density is an important aspect of performance behavior so that its theoretical calculations are indispensable in recognizing energetic materials of interest. Some empirical methods were recently introduced for reliable detonation and thermochemical properties of ideal and non-ideal pure or mixed explosives of different classes [1–12]. However, density of energetic material has an important role in predicting its detonation pressure and velocity. Crystalline or maximum nominal density would be usually needed to obtain the highest predicted detonation performance of any new energetic compounds, by a computer code such as CHEETAH [13] or various empirical methods [14].

The molecular structure, elemental composition, heat of formation, solid state density and microstructure are important properties characterizing the performance of an energetic material. Microstructure shows the three-dimensional structure with various types of dislocations and imperfections. The molecular microstructures are the factors that affect the sensitivity of a material in response to impact or shock stimuli. Density of organic compounds can be calculated on the fundamental basis if all inter- or intramolecular forces are known. To calculate density of an energetic compound, the complex theoretical approach uses quantum chemistry for determining detailed information about the crystal structure [15–19]. Another convenient method for estimating the density of energetic materials is based on summing up the volume of each atom or molecular fragment [20–24]. Group or volume additivity for density predictions of energetic materials is truly a back-of-the-envelope or spread sheet calculation and involves the summation of the appropriate atom and functional group volumes to give an effective condensed-state volume for a molecule, then density.

It should be mentioned that increasing the oxygen balance and heat of formation will generally increase the sensitivity of an explosive as well as the performance. Since detonation pressure is proportional to the square of the density, increasing density should do more to improve the performance. Thus, density is one of the primary physical parameter in detonation performance [1,4]. The purpose of this work is to show some simple equations for predicting density of acyclic and

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cyclic nitramines, nitrate esters and nitroaliphatic compounds. The new correlations will be applied to some of common and recently synthesized $C_aH_bN_cO_d$ explosives. To show the reliability of predicted values as compared to well-known different additivity group methods, the method of Tarver [23] is also used for some explosives. The introduced models will be very valuable in directing research efforts towards design of complicated molecular structure of high-density explosives because the calculated density could be meaningful in the decision as to whether it is worth the effort to attempt a new and complex synthesis.

2. Determination of density of nitrate esters and nitroaliphatic compounds

One of the fundamental goals in the field of organic explosives is to develop methods for predicting the performance of new explosives before synthesis which requires the density and the heat of formation of the explosive. However, the main intent in this work was to investigate a generalized simple method for density prediction of several classes of $C_aH_bN_cO_d$ explosives. It was noticed that the results predicted by this method are comparable with more complicated quantum mechanical computations as well as group additivity procedure.

The study on acyclic and cyclic nitrate esters and nitroaliphatic systems shows the atomic composition and the number of special functional groups can be integrated into an empirical formula to predict density of proposed explosive. The general formula based on this assumption for $C_aH_bN_cO_d$ acyclic and cyclic nitrate esters and nitroaliphatic compounds can be written as

$$\rho_0 = \frac{Aa + Bb + Cc + Dd + \sum n_i(\mathrm{FG})_i}{M_\mathrm{W}} \quad (1)$$

where A, B, C, D and $(\mathrm{FG})_i$ are adjustable parameters for elemental composition and specified functional groups (FG = functional group), M_W the molecular weight of the explosive, ρ_0 density of explosive, and n_i is the number of functional groups. To obtain adjustable coefficients of Eq. (1), experimental data of Table 1 were used. Since the presence of functional groups of alcohols, esters and ethers (–OH, –C(=O)O– and –O–) shows an appreciable effect on the molecular forces and packing of molecules in a given volume with respect to the other functional groups, the following equation can be obtained as a core correlation by optimizing adjustable coefficients for acyclic and cyclic nitrate ester and nitroaliphatic compounds:

$$\rho_0 = \frac{47.9732a - 19.2948b + 26.5340c + 26.0011d - 25.3190n_\mathrm{COO} - 0.6358n_\mathrm{O} + 11.5413n_\mathrm{OH}}{M_\mathrm{W}} \quad (2)$$

where n_COO, n_O and n_OH are the number of esters, ethers and alcohols functional groups.

Multiple linear regression method [25] was also used to find adjustable parameters. The left-division method for solving linear equations uses the least squares method because the equation set is overdetermined [25]. This correlation would be corrected for some specific cases according to certain molecular structure as below:

(a) Mononitroalkanes:

$$\rho_{0,\mathrm{corr}} = 0.4170 + 0.5970\rho_0 \quad (2a)$$

(b) Two $–NO_2$ groups attached to one carbon (without mentioned functional groups):

$$\rho_{0,\mathrm{corr}} = 0.1233 + 0.8373\rho_0 \quad (2b)$$

(c) Three $–NO_2$ groups attached to one carbon:

$$\text{if } n_{\mathrm{CH_2}} \geq 1.5n_{\mathrm{NO_2}} \text{ then } \rho_{0,\mathrm{corr}} = 3.033 - \rho_0 \quad (2c)$$

$$\text{if } n_{\mathrm{CH_2}} \leq 0.6n_{\mathrm{NO_2}} \text{ then } \rho_{0,\mathrm{corr}} = -0.3788 + 1.2569\rho_0 \quad (2c')$$

For those molecules that satisfy both conditions b and c, Eqs. (2c) and (2c′) rather than (2b) should be used.

(d) For nitrate systems (without cyclic ring attachment), if $n_{\mathrm{CH_2ONO_2}} + n_{\mathrm{CHONO_2}} \geq 4$:

$$\rho_{0,\mathrm{corr}} = 0.1745 + 0.9235\rho_0 \quad (2d)$$

(e) Cage and cyclo-nitro compounds in which only one $–NO_2$ (not more) attached to carbon atom:

$$\rho_{0,\mathrm{corr}} = -0.0515 + 0.9142\rho_0. \quad (2e)$$

3. Determination of density of cyclic and acyclic nitramine compounds

The study showed that there is no need to use the effect of the other functional groups as in Eq. (1) for cyclic and acyclic nitramines because it seems that $N–NO_2$ group has predominant effect in packing of molecules. Experimental data of Table 2 were used to find coefficients of Eq. (1) in this situation. Thus, two optimized new correlations for calculating density of cyclic (and the compounds in which $N–NO_2$ attached to an aromatic ring such as tetryl) and acyclic nitramines are introduced as the following forms, respectively:

$$\rho_{0,\mathrm{cyclic}} = \frac{13.1466a - 5.3031b + 39.7241c + 29.3395d}{M_\mathrm{W}} \quad (3)$$

$$\rho_{0,\mathrm{acyclic}} = \frac{66.8566a - 27.3717b + 52.9597c + 12.8071d}{M_\mathrm{W}} \quad (4)$$

Correlation (3) can be applied only for polycyclic energetic compounds that contain no more than one oxygen in their cyclic structures.

4. Results and discussion

The above correlations provide a new method to estimate the density of some well-known classes of explosives, which requires as input only the elemental compositions and some specified functional groups. The output of these correlations