Quick estimation of heats of detonation of aromatic energetic compounds from structural parameters

Mohammad Hossein Keshavarz *

Department of Chemistry, Malek-Ashtar University of Technology, Shahin-Shahr, P.O. Box 83145/115, Islamic Republic of Iran

Abstract

In this paper, a simple procedure is introduced for a quick and reliable estimation of detonation heats of aromatic energetic compounds without considering heats of formation of energetic compounds. This method does not use any experimental or computed data of energetic materials. The methodology assumes that the heat of detonation of an energetic compound with composition of $C_aH_bN_cO_d$ can be obtained from the number of nitrogens, ratios of oxygen to carbon and hydrogen to oxygen as well as the contribution of some specific functional groups. There is no need to use any assumed decomposition products to calculate heats of detonation for energetic compounds. Predicted heats of detonation of pure energetic compounds with the product H_2O in the liquid state for 31 aromatic energetic compounds have a root mean square (rms) of deviation of 0.32 kJ/g from experiment. The new method gives good results with respect to two empirical methods which use measured heats of formation of explosives with two sets of decomposition gases.
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1. Introduction

Detonation parameters such as pressure and velocity can be computed using complicated computer codes such as CHEE-TAH [1]. Typical inputs to these computations are the heat of formation and initial density of the explosive and the equations of state, e.g. the Jacobs–Cowperthwaite–Zwisler (JCZ) [2,3]. The computation of the performance of energetic materials by the usual thermo-chemical/hydrodynamic computer codes are highly tedious, often requiring intricate balancing of chemical equations. Detonation parameters can also be calculated by some empirical methods [4]. Detonation pressure for ideal explosives, as an example, can be evaluated by different methods such as heat of detonation at loading density greater than 1 g/cm³ [5–7] or any loading density [8], approximate detonation temperature [9–12] and gas phase heat of formation of explosive [13].

Heat of detonation is one of the important detonation parameters that can be used as the energy available to do mechanical work and estimating potential damage to surroundings [14].

Though it may be measured experimentally or calculated from theory, theoretical calculations are useful in comparing the relative heat releasing of one explosive with respect to another. Moreover, it can also be used to determine detonation pressure and velocity of explosives via assumed different decomposition pathways [5–8,15]. Predicting fairly simple and accurate heats of detonation, by simple empirical methods, are desired to determine the performance of energetic compounds.

The purpose of this work is to introduce a simple method to predict the heats of detonation of aromatic energetic compounds from their specific structural parameters. This work assumes that the number of nitrogens, ratios of oxygen to carbon and hydrogen to oxygen as well as the contribution of some functional groups are sufficient for reliable prediction of heats of detonation as compared to the other available empirical methods. The calculated heats of detonation will be applied to 31 CHNO energetic compounds and compared the results with measured data as well as two empirical methods, namely Kamlet and Jacobs (K&J) [5] as well as Keshavarz and Pouretedal (K&P) [8] methods. It will be shown that the new method is much simple in form and easy to use in a practical sense for quick calculations and screening of notional energetic materials without using any experimental data.

* Tel.: +98 312 522 5071; fax: +98 312 522 5068.
E-mail addresses: mhkir@yahoo.com, mhkeshavarz@mut-es.ac.ir.

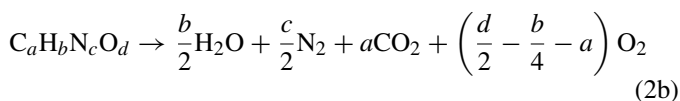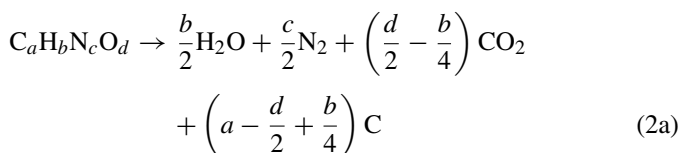## 2. Different methods for calculating heats of detonation

Predicting various thermochemical and performance properties of new energetic materials is an important problem to the scientific community concerning synthesis, formulation and applications of energetic materials. The improvement of simple and reliable empirical methods can increase capabilities to predict various properties of notional energetic materials that are associated with the performance before expending resources. Since manufacturing and testing of a new energetic compound is very expensive in time and money, simple empirical methods can be a proper tool to predict initial guess.

The heat of detonation, Q, defined as the negative of the enthalpy change of the detonation reaction, can be determined from the heats of formation of reactants and decomposition products as following [5]:

$$Q \cong -\frac{\Delta H_f \text{ (detonation products)} - \Delta H_f \text{ (explosive)}}{\text{formula weight of explosive}} \quad (1)$$

Decomposition of an explosive is extremely fast, which will in turn cause them to expand and work on surroundings; it will raise the temperature of gaseous products. If the heat of formation of an energetic compound is known, then using the standard heats of formation of assumed detonation products will lead to predict heat of detonation. As seen in Eq. (1), a positive heat of formation (per unit weight) leads to a greater release of energy upon detonation. To use Eq. (1), experimental or calculated condensed phase heats of formation of energetic compounds as well as the assumed or computed equilibrium composition of gaseous products would be needed. Some new procedures have been recently introduced for reliable estimation of condensed phase heat of formation of selected classes of explosives [16–18].

Kamlet and coworkers [5–7], in an effort to match the experimentally determined values of detonation pressure and velocity through computational and empirical methods, introduced N_2, H_2O, CO_2 (but not CO) as the important products of decomposition reaction. For an explosive with the general formula $C_aH_bN_cO_d$, they introduced the following overall stoichiometry for underoxidized and overoxidized explosives:

$$C_aH_bN_cO_d \rightarrow \frac{b}{2}H_2O + \frac{c}{2}N_2 + \left(\frac{d}{2} - \frac{b}{4}\right)CO_2$$
$$+ \left(a - \frac{d}{2} + \frac{b}{4}\right)C \quad (2a)$$

$$C_aH_bN_cO_d \rightarrow \frac{b}{2}H_2O + \frac{c}{2}N_2 + aCO_2 + \left(\frac{d}{2} - \frac{b}{4} - a\right)O_2 \quad (2b)$$

They used experimental condensed phase heats of formation of explosives in Eq. (1) to calculate their heats of detonation. Rice and Hare [14] used the predicted product concentrations by the CHEETAH 2.0/JCZS to compute heats of detonation using quantum mechanical calculations because thermochemical calculations show CO is a major component of gaseous products. Predicted heats of detonation proposed by decomposition products of the CHEETAH 2.0/JCZS have a root mean square (rms) of deviation smaller than Kamlet and Jacobs (K&J)

[5] method. To compute heats of detonation, Rice and Hare [14] used complicated quantum chemistry code GAUSSIAN 98 [19] which has some difficulties such as time and computer limitations. Keshavarz and Pouretedal (K&P) [8] introduced four different pathways to determine detonation products. Oxygen content of explosives can give the other detonation products such as CO and H_2 for oxygen lean explosives [8]. The calculated heats of detonation by this method are better than those obtained by K&J procedure [8] but two methods require condense phase heat of formation of explosive. Later, it is shown that the heat of detonation can be correlated with the explosive's elemental composition and estimated gas phase heat of formation of the explosive [23]. This method uses additivity rules of atomic and molecular groups, such as the methods of Benson et al. [20], Yoneda [21], Reid et al. [22], etc., to calculate gas phase heats of formation. The results of this procedure are comparable with K&P outputs [8]. However, all of empirical methods require measured or calculated heat of formation of energetic compound.

The study of heats of detonation on various aromatic energetic compounds shows that it is possible to provide the simplest correlation of heats of detonation only from some structural parameters. To find a good relationship of heats of detonation as a function of suitable structural parameters, various situations were studied and optimized with experimental data. It is found that the number of nitrogens, the ratios of oxygen to carbon and hydrogen to oxygen have important effects because they can determine the formation of different possible decomposition products. Moreover, the contributions of some specific functional groups can affect the values of heats of detonation of various aromatic energetic compounds. However, the general form of correlation based on mentioned parameters can be given as

$$Q = Z_1 + Z_2 n_N + Z_3 R_{O/C} + Z_4 R_{H/O} + Z_5 C_{SFG} \quad (3)$$

where Z_1–Z_5 are adjustable parameters, $R_{O/C}$ and $R_{H/O}$ the ratios of oxygen to carbon and hydrogen to oxygen, respectively, n_N the number of nitrogens and C_{SFG} is the contribution of some specific functional groups in aromatic CHNO energetic compounds. Experimental data of various pure aromatic energetic compounds, which are listed in Table 1, were used to find adjustable parameters. Multiple linear regression method [24] was used to find adjustable parameters. Since the equation set is overdetermined [24], the left-division method for solving linear equations uses the least squares method. Optimized correlation can be given as follows:

$$Q(\text{kJ g}^{-1}) = 2.129 + 0.178 n_N + 0.874 R_{O/C} + 0.160 R_{H/O}$$
$$+ 0.965 C_{SFG} \quad (4)$$

To use this correlation, $C_{SFG} = -1$ for aromatic energetic compounds that have some specific functional groups, namely –COOH, NH_4^+, two –OH (or one –OH with one –NH_2) and three –NH_2. Eq. (4) can predict heats of detonation of pure energetic compounds with H_2O in liquid state. Heats of detonation of 31 aromatic energetic compounds, where experimental data are available [25], are calculated and compared with the
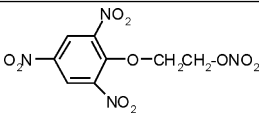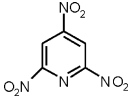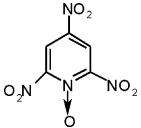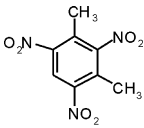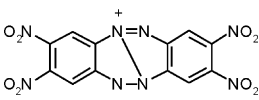
Table 1
Comparison of the calculated heats of detonation of Eq. (3), K&J [5] and K&P [8] methods with measured values [25]

Name of energetic compound	Structure	Q_{exp} (kJ/g)	Q_{new} (kJ/g)	Dev_{new}	$Q_{K\&J}$ (kJ/g)	$Dev_{K\&J}$	Q_{KP} (kJ/g)	$Dev_{K\&P}$
Ammonium picrate		2.871	3.033	−0.16	5.115	−2.24	2.288	0.58
Dinitronaphtalene(1,8)		3.064	3.075	−0.01	5.011	−1.95	2.201	0.86
Dinitronaphtalene(1,5)		3.031	3.075	−0.04	4.978	−1.95	2.168	0.86
Dinitroorthocresol		3.027	3.301	−0.27	5.310	−2.28	1.782	1.25
Dinitrotoluene(2,4)		3.192	3.225	−0.03	5.420	−2.23	2.055	1.14
Dinitrotoluene(2,6)		3.325	3.225	0.10	5.554	−2.23	2.188	1.14
Ethyl picrate		3.515	3.588	−0.07	5.792	−2.28	2.230	1.29
Ethyl tetryl		4.058	4.033	0.02	6.207	−2.15	2.879	1.18
2,4,6,2′,4′,6′-Hexanitrodiphenylamine (HNDP)		4.075	4.316	−0.24	5.980	−1.91	3.117	0.96
Hexanitrostilbene		4.088	4.027	0.06	6.015	−1.93	3.123	0.97
Metadinitrobenzene		2.666	3.228	−0.56	5.585	−2.92	2.470	0.20
Picramic acid		2.674	2.587	0.09	4.816	−2.14	1.531	1.14
Picric acid		3.437	3.751	−0.31	5.513	−2.08	3.059	0.38

Table 1 (*Continued*)

Name of energetic compound	Structure	Q_{exp} (kJ/g)	Q_{new} (kJ/g)	Dev_{new}	$Q_{K\&J}$ (kJ/g)	$Dev_{K\&J}$	Q_{KP} (kJ/g)	$Dev_{K\&P}$
Polynitropolyphenylene		3.200	3.564	−0.36	6.026	−2.83	3.363	−0.16
Styphnic acid (TNR)		2.952	2.923	0.03	4.835	−1.88	2.901	0.05
Tetranitroaniline		4.378	4.245	0.13	6.076	−1.70	4.341	0.04
Tetryl		4.773	4.118	0.65	6.331	−1.56	3.764	1.01
2,4,6-Trinitrotoluene (TNT)		4.564	3.546	1.02	5.888	−1.32	2.628	1.94
1,2-Diamino-2,4,6-trinitrobenzene (DATB)		4.100	4.027	0.07	5.369	−1.27	2.324	1.78
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)		3.062	3.267	−0.20	5.071	−2.01	2.030	1.03
Trinitroaniline		3.589	3.822	−0.23	5.592	−2.00	2.540	1.05
Trinitroanisol		3.777	3.651	0.13	5.955	−2.18	2.555	1.22
1,3,5-Trinitrobenzene (TNB)		3.964	3.617	0.35	5.966	−2.00	2.911	1.05
Trinitrobenzoic acid		3.008	2.757	0.25	5.076	−2.07	2.556	0.45
2,4,6-Trinitrocresol		3.370	3.651	−0.28	5.547	−2.18	2.147	1.22
Trinitronaphtalene		3.521	3.321	0.20	5.547	−2.03	2.732	0.79

Table 1 (*Continued*)

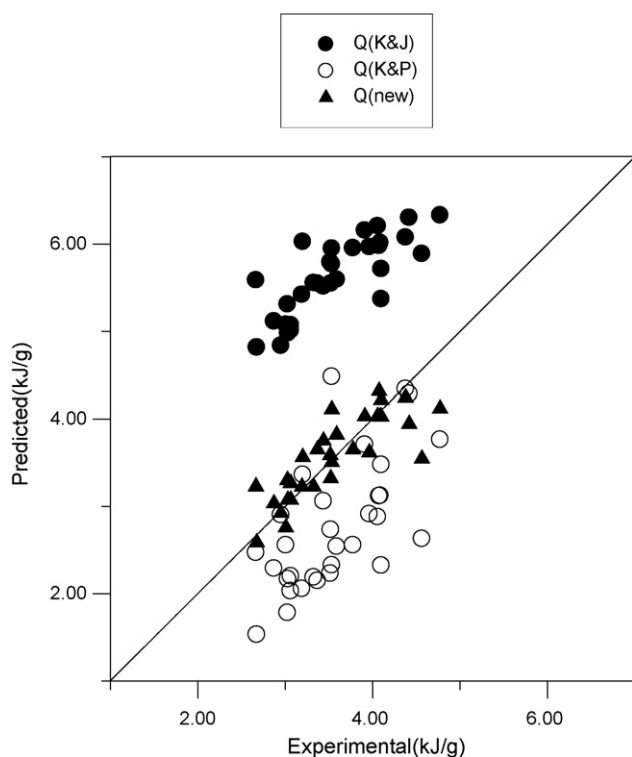| Name of energetic compound	Structure	Q_{exp} (kJ/g)	Q_{new} (kJ/g)	Dev_{new}	$Q_{K\&J}$ (kJ/g)	$Dev_{K\&J}$	Q_{KP} (kJ/g)	$Dev_{K\&P}$
Trinitrophenoxethylnitrate		3.911	4.030	−0.12	6.156	−2.25	3.708	0.20
Trinitropyridine		4.418	3.943	0.47	6.302	−1.88	4.286	0.13
Trinitropyridine-*N*-oxide		3.533	4.110	−0.58	5.950	−2.42	4.479	−0.95
2,4,6-Trinitroxylene		3.533	3.505	0.03	5.768	−2.24	2.327	1.21
Tacot		4.100	4.217	−0.12	5.714	−1.61	3.476	0.62
rms deviation				0.32		2.08		0.99

Fig. 1. Predicted heats of detonation [$H_2O(l)$] vs. experimental values for CHNO energetic compounds. The solid lines represent exact agreement between predictions and experiment. Solid and hollow circles denote calculated heats of detonation by K&J and K&P methods, respectively. Filled triangles denote calculated results of new method.

experimental values as well as K&J [5] and K&P [8] methods. To compare the results of different methods, deviation of measured values from calculated values are also given in Table 1. As shown, the rms results of the new method are surprisingly much lower than two mentioned empirical methods. A visual comparison of the predictions with experiment is given in Fig. 1. Fig. 1 shows the comparison between experiment and predictions in which the H_2O product in liquid state. As evident in Fig. 1, the new method shows the best agreement with experimental data. Although K&J [5] and K&P [8] methods require knowledge of measured or estimated condensed phase heat of formation of the explosive, the new method is based on only some structural parameters. Thus, this may be taken as appropriate validation test of the new method for aromatic energetic materials.

3. Conclusions

Development of simple methods for predicting various properties of new energetic materials before synthesis could be important for economically and time saving process. However, the main intent in this work was to investigate the likelihood of a generalized simple method for predicting heats of detonation of aromatic CHNO energetic compounds of somewhat more practical importance to the explosive user. The introduced correlation is much simple for rapid desk calculations of heats of detonation of aromatic energetic compounds with about the same reliance on their answers as one use the best empirical methods. The new method requires no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties of explosive and assumed detonation products. As

seen in Table 1, good agreement is obtained for the new procedure with measured data as compared to K&J [5] and K&P [8] methods. Moreover, there is no need to know heats of formation of energetic compounds, which are usually fundamental inputs in the available methods.

Acknowledgements

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