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Simple procedure for determining heats of detonation

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Abstract

A simple approach is introduced for calculating heats of detonation via composition of explosive and its gas phase heat of formation that can be calculated by group additivity rule. There is no need to use any experimental and computed data of explosive. Two correlations are introduced for desk calculation of heat of detonation of aromatic and non-aromatic explosive compound that contains the elements of carbon, hydrogen, nitrogen and oxygen. Predicted heats of detonation for 37 explosives have a root mean square (r.m.s.) of deviation for experiment of 0.64 kJ/g, which show good agreement with respect to measured values for oxygen-lean and oxygen-rich explosives.

Keywords: Performance; Heat of detonation; Gas phase heat of formation; Correlation

1. Introduction

Since predicting the performance of new energetic materials is a problem of the utmost importance for a chemist concerning synthesis and formulation, the development of simple reliable methods can improve capabilities to predict various properties of notional energetic materials that are associated with the performance before expending resources. Elimination of any poor candidate due to performance problems through predictive methods is highly desirable because it is time-saving, cost-effective and environmentally desirable at early stage of development.

Detonation pressure and velocity as well as detonation energy or heat of detonation have been regarded as the principal measures of performance of detonating explosives for many years. These parameters can be calculated by a complicated computer code, e.g. CHEETAH [1], when the heat of formation and the density of the explosive substance are known and the equations of state for the detonation products are assumed. Some of well-known equations of state such as Becker–Kistiakosky–Wilson (BKW) [2], the Jacobs–Cowperthwaite–Zwisler (JCZ) [3,4], Kihara–Hikita–Tanaka (KHT) [5] and Exp-6 [6] for gaseous detonation products. Furthermore, some empirical methods have been introduced for determination of the detonation performance of ideal and less ideal pure or mixture of different classes of explosives that attempt to relate chemical structure and either theoretical maximum density or loading density with detonation parameters [7–15].

Heat of detonation can be used as the energy available to do mechanical work and estimating potential damage to surroundings [16]. Its calculated values can be used to determine detonation pressure and velocity of explosives via assumed different decomposition pathways [7,15]. The empirical methods for calculating heat of detonation require condense heat of formation which can be measured or estimated [16,17] for some classes of explosives. Quantum mechanical information about a single explosive can also be used to evaluate heat of detonation [18]. Although root mean square (r.m.s.) of deviation of quantum mechanical calculations are less than ones predicted by empirical methods but they have special complexity and take much time for optimization of large system. The purpose of this work was to correlate heat of detonation with the explosive's elemental composition and

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simply estimated gas phase heat of formation of the explosive by additivity rules of some group estimation gas phase heat of formation of the explosive related to the molecular structure, e.g. the methods of Benson [20], Yoneda [21], Joback [22], etc. This work assumes that the heat of detonation of an explosive with composition $C_aH_bN_cO_d$ can be determined from the elemental composition and estimates its heat content in gas phase. There is no need to estimate the composition of detonation products which are usually necessary for all of mentioned methods. Two empirical equations will be introduced that correlate directly the elemental composition of the explosive and its estimated gas phase heat of formation with heat of detonation for aromatic and non-aromatic explosives. The results will be compared with two empirical methods for 37 explosives. It should be noted that results predicted by this very simple method are comparable with outputs from complicated computations [16] and the accuracy is not necessarily enhanced by greater complexity. However, since the values of condensed heat of formation are hardly known experimentally for new explosives of interest which are needed for pervious empirical methods [7,15], the present method can be used to estimate their heat of detonation without any difficulties.

2. Initial knowledge

The heat librated by detonation will raise the temperature of gases detonation because decomposition of an explosive is extremely fast, which will in turn cause them to expand and work on surroundings. However, the effectiveness of an explosive depends on the amount of energy available in it and the rate of release of available energy when detonation occurs. A positive heat of formation (per unit weight) is favorable for an explosive because this leads to a greater release of energy upon detonation and an improvement in performance. A quick estimate of the heat of detonation can be determined from the heats of formation of the reactants and the products of detonation through the relation:

$$Q \cong \frac{-[\Delta H_\mathrm{f}(\text{detonation products}) - \Delta H_\mathrm{f}(\text{explosive})]}{\text{formula weight of explosive}} \tag{1}$$

The assumed or computed equilibrium composition of the product gases can be used for evaluating the heat of formation of detonation products. If the condensed heat of formation of the explosive and decomposition products of explosive are known, then using the standard heats of formation of gaseous products will lead to the prediction of the heat of detonation of an explosive. Kamlet and Jacobs [7], in an effort to analyse and understand the formidable appearance of the data of many computations for a wide variety CHNO explosives, introduced N_2, H_2O, CO_2 (but not CO) as the important products of decomposition reaction. Since thermochemical calculations show CO is a major component of gaseous products, Rice and Hare [16] used the predicted product concentrations by the CHEETAH 2.0/JCZS for computing heat of detonation using quantum mechanical calculations. Their result with the product H_2O in liquid state, corresponds to two sets of decomposition gases proposed by Kamlet and Jacobs and by the CHEETAH 2.0/JCZS, have a r.m.s. deviation small from experiment by counting CO as major product. Calculations of heat of detonation by using quantum chemistry codes such as Gaussian 98 [23] in addition to their complexities have some difficulties such as time and computer limitations. Recently, four different pathways were introduced for determining detonation products of explosives which counted the other detonation products such as CO and H_2 for oxygen-lean explosives [15]. The calculated heat of detonation by this method is better than those obtained by Kamlet and Jacobs procedure [15].

Though heat of detonation may be measured experimentally or calculated from theory, theoretical calculations are useful in comparing the relative heat releasing of one explosive with another. The calculation of the performance of energetic materials by the usual thermochemical methods such as CHEETAH [1] is highly tedious, often requiring intricate balancing of chemical equations. Predicting fairly accurate heats of detonation, by simple empirical methods, are highly desired for calculating the various parameters of energetic compounds because they can correlate with detonation pressure and velocity.

3. Results and discussion

It is proposed here that the heat of detonation of a high explosive as one of detonation parameters can most appropriately be expressed as its elemental composition and heat content in gas phase rather than condensed phase. Rothstein and Petersen [8,9] and Stine [10,11] also used only elemental composition of explosive without using assumed or calculated detonation products to calculate detonation velocities. Since crystalline heat of formation can correlate with gas phase heat of formation for some classes of explosives [19], crystal effects can be excluded for determining the performance in this manner [12,13]. The results indicated that the following general equation is suitable for $C_aH_bN_cO_d$ explosive with five adjustable parameters X_1–X_5 in it:

$$Q_\mathrm{d}\,(\mathrm{kJ/g}) = \frac{X_1a + X_2b + X_3c + X_4d + X_5\Delta H_\mathrm{f}^\circ(\mathrm{g})}{\mathrm{MW}} \tag{2}$$

where MW and $\Delta H_\mathrm{f}^\circ(\mathrm{g})$ are molecular weight of explosive and its calculated gas phase heat of formation by additivity rules respectively. Experimental heats of detonation of aromatic and non-aromatic explosives [24], with the H_2O in liquid state, are used to find mentioned adjustable parameters. The results show that two optimized correlations (3) and (4) can be obtained for non-aromatic and aromatic explosives, respectively:

$$Q_{\rm d}\,({\rm kJ/g}) = \frac{\begin{array}{l}58.722a - 55.011b - 21.234c + 250.92d\\ +4.485\Delta H_{\rm f}^{\circ}({\rm g})\end{array}}{\rm MW} \tag{3}$$

$$Q_{\rm d}\,({\rm kJ/g}) = \frac{\begin{array}{l}61.781a - 51.317b + 30.656c + 91.446d\\ -0.2791\Delta H_{\rm f}^{\circ}({\rm g})\end{array}}{\rm MW} \tag{4}$$

The correlations can be applied to the oxygen-lean as well as oxygen-rich explosives. As seen, Eqs. (3) and (4) require no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties of explosive and assumed detonation products other than simply calculated gas phase heat of formation by additivity rule.

The calculated gas phase heats of formation of explosives by additivity rule and the other necessary data are shown in Table 1. Calculated heats of detonation are given in Table 2 and compared with corresponding measured values and two empirical methods [7,15]. Difference of predictions from experiments, e.g. Dev = measured − predicted, for various methods are given in Table 2. The root mean square (r.m.s.) of deviations also given in Table 2 which can be defined as

$$\text{r.m.s. deviation}\,({\rm kJ/g}) = \sqrt{\frac{1}{N}\sum_{i=1}^{N}{\rm Dev}_i^2} \tag{5}$$

where N represents the number of heat of detonation measurements, namely 37. The new procedure, which is based on simply hand calculated gas phase heats of formation and

Table 1
Parameters used in calculations

Explosive	Chemical formula	Condensed phase[a], $\Delta H_{\rm f}$ (kcal/mol)	Gas phase[b], $\Delta H_{\rm f}$ (kJ/mol)
HMX	$C_4H_8N_8O_8$	17.92	45.02
RDX	$C_3H_6N_6O_6$	15.99	37.85
TNT	$C_7H_5N_3O_6$	−16.03	−4.30
PETN	$C_5H_8N_4O_{12}$	−128.8	−174.3
TETRYL	$C_7H_5N_5O_8$	4.79	9.28
DATB	$C_6H_5N_5O_6$	−23.6	14.06
NG	$C_3H_5N_3O_9$	−88.6	−129.6
NQ	$CH_4N_4O_2$	−22.2	50.40
TATB	$C_6H_6N_6O_6$	−33.4	19.40
BTNEU	$C_5H_6N_8O_{13}$	−76.91	−55.96
DEGN	$C_4H_8N_2O_7$	−104.4	−130.0
DINA	$C_4H_8N_4O_8$	−65.88	−84.83
DIPEHN	$C_{10}H_{16}N_6O_{19}$	−233.8	−300.4
Ethriol trinitrate	$C_6H_{11}N_3O_9$	−114.8	−144.5
EDNA	$C_2H_6N_4O_4$	−24.81	0.19
Ethyl nitrate	$C_2H_5NO_3$	−45.45	−54.37
MHN	$C_6H_8N_6O_{18}$	−152.03	−249.9
Methyl nitrate	CH_3NO_3	−37.2	−49.44
Nitroethane	$C_2H_5NO_2$	−32.03	−22.78
NM	CH_3NO_2	−27.01	−17.85
Nitrourea	$CH_3N_3O_3$	−67.53	−23.90
PETRIN	$C_5H_9N_3O_{10}$	−133.98	−175.9
TEGN	$C_6H_{12}N_2O_8$	−150.3	−171.4
Dinitroorthocresol	$C_7H_6N_2O_5$	−47.8	−41.34
Ethylpicrate	$C_8H_7N_3O_7$	−48.02	−40.81
Ethyltetryl	$C_8H_7N_5O_8$	−4.31	4.338
HNDP	$C_{12}H_5N_7O_{12}$	9.88	24.4
Hexanirostilbene	$C_{14}H_6N_6O_{12}$	18.679	−6.51
Picramic acid	$C_6H_5N_3O_5$	−59.33	−23.08
TNR	$C_6H_3N_3O_8$	−125	−81.34
TNA	$C_6H_3N_5O_8$	−11.69	3.40
Trinitroanisol	$C_7H_5N_3O_7$	−36.61	−35.88
TNB	$C_6H_3N_3O_6$	−10.4	3.38
Trinitrobenzoic acid	$C_7H_3N_3O_8$	−96.31	−87.97
2,4,6-Trinitrocresol	$C_7H_5N_3O_7$	−60.29	−46.65
Trinitrophenoxethylnitrate	$C_8H_6N_4O_{10}$	−66.31	−74.97
TNX	$C_8H_7N_3O_6$	−24.53	−11.96

[a] Heat of formation of pure explosives were obtained from [24].

[b] Heat of formation calculated by Joback additive group procedure [22].

Table 2
Comparison of calculated heats of detonation of the new correlations with two empirical methods, namely Kamlet and Jacobs (KJ) [7], and Keshavarz and Pouretedal (KP) [15] methods as well as measured values [24]

Explosive	Q_{exp} (kJ/g)	Q_{new} (kJ/g)	Dev_{new}	Q_{KJ} (kJ/g)	Dev_{KJ}	Q_{KP} (kJ/g)	Dev_{KP}
HMX	6.197	6.20	0.00	6.78	−0.58	5.61	0.58
RDX	6.322	6.28	0.04	6.82	−0.50	5.66	0.66
TNT	4.564	3.60	0.96	5.89	−1.32	2.63	1.94
PETN	6.322	6.32	0.00	6.89	−0.57	6.35	−0.03
TETRYL	4.773	3.69	1.09	6.33	−1.56	3.76	1.01
DATB	4.100	3.34	0.76	5.37	−1.27	2.32	1.78
NG	6.671	6.67	0.00	7.15	−0.48	6.72	−0.05
NQ	3.071	4.63	−1.56	4.61	−1.54	2.92	0.15
TATB	3.062	3.06	0.00	5.07	−2.01	2.03	1.03
BTNEU	6.454	7.27	−0.81	6.49	−0.03	6.49	−0.03
DEGN	4.566	4.72	−0.16	6.62	−2.05	4.40	0.16
DINA	5.458	5.57	−0.11	6.90	−1.44	5.46	0.00
DIPEHN	5.143	5.72	−0.58	6.63	−1.49	5.15	−0.01
Ethriol trinitrate	4.244	4.81	−0.56	6.62	−2.38	3.87	0.37
EDNA	4.699	4.71	−0.01	6.34	−1.64	4.60	0.10
Ethyl nitrate	4.154	3.63	0.53	6.85	−2.69	3.48	0.67
MHN	6.384	7.04	−0.65	7.22	−0.83	6.35	0.03
Methyl nitrate	6.748	5.24	1.51	7.38	−0.63	6.82	−0.08
Nitroethane	1.686	2.94	−1.26	6.43	−4.75	1.16	0.52
NM	4.821	4.82	0.00	6.79	−1.97	4.65	0.17
Nitrourea	3.745	4.53	−0.78	4.20	−0.46	3.79	−0.05
PETRIN	5.230	5.37	−0.14	6.67	−1.44	5.24	−0.01
TEGN	3.317	3.70	−0.38	6.17	−2.85	2.53	0.79
Dinitroorthocresol	3.027	3.31	−0.28	5.31	−2.28	1.78	1.24
Ethylpicrate	3.515	3.42	0.10	5.79	−2.28	2.23	1.28
Ethyltetryl	4.058	3.38	0.67	6.21	−2.15	2.88	1.18
HNDP	4.075	4.08	0.00	5.98	−1.91	3.12	0.96
Hexanirostilbene	4.088	4.09	0.00	6.02	−1.93	3.12	0.97
Picramic acid	2.674	3.37	−0.69	4.82	−2.14	1.53	1.14
TNR	2.952	4.34	−1.39	4.83	−1.88	2.90	0.05
TNA	4.378	4.03	0.35	6.08	−1.70	4.34	0.04
Trinitroanisol	3.777	3.78	0.00	5.95	−2.18	2.56	1.22
TNB	3.964	4.02	−0.06	5.97	−2.00	2.91	1.05
Trinitrobenzoic acid	3.964	4.38	−0.42	5.08	−1.11	2.56	1.41
2,4,6-Trinitrocresol	3.370	3.79	−0.42	5.55	−2.18	2.15	1.22
Trinitrophenoxethylnitrate	3.911	3.91	0.00	6.16	−2.24	3.71	0.20
TNX	3.533	3.23	0.30	5.77	−2.24	2.33	1.21
r.m.s. deviation (kJ/g)		0.64		1.90		0.85	

the other parameters, show surprisingly very good agreement with experimental values as indicated in Table 2. This may be taken as appropriate validation tests of the new method with $C_aH_bN_cO_d$ explosives. Since for most of subject explosives, the $|\Delta H_f^\circ(g)|$ of the explosive is small relative to the elemental composition of the $C_aH_bN_cO_d$ explosive, no precise prediction of gas phase heat of formation was required in order to reproduce the experimental data within the error limits ascribed to that of data.

One important aspect of the present work is that easily hand calculated gas phase heat of formation of explosive can be used to determine heat of detonation. Two empirical correlations were introduced for aromatic and non-aromatic explosives. The method can be applied for a wide range of explosives including under-oxidized and over-oxidized explosives. As shown in Table 2, the r.m.s. results of the new method were compared with the predictions of two empirical methods [7,15]. Two later empirical methods [7,15] assume that the heat of detonation of an explosive can be approximated as the difference between the heats of formation of detonation products and that of explosive formulation divided by the formula weight of the explosive. As seen, although the r.m.s. predicted by Keshavarz and Pouretedal (KP) method [15] is much lower than those obtained by Kamlet and Jacobs (KJ) [7] procedure but r.m.s. of new simple method surprisingly is lower than KP method. Furthermore, two empirical KP and KJ methods require knowledge of measured or estimated condensed heat of formation of explosive.

It should be mentioned that the method is usable for many new explosives; especially heterocyclic compounds have received a great amount of interest [25] in recent years. CL-20 is the most studied example of highly nitrated cage that is the most powerful explosive being investigated at the pilot scale or lager [25]. Predicted heat of detonation for CL-20 is

6.90 kJ/g ($\Delta H_f(g) = 54.07$ kJ/mol), which is consistent with recently reported value 6.234 kJ/g [26]. As another useful example, 2,4,6-trinitro-1,3,5-triazine can be introduced theoretically as an interesting high-energy density material which may be used as the most powerful energetic material [27,28]. According to Eq. (4), its calculated $\Delta H_f(g) = 174.3$ kJ/mol gives $Q_d = 4.20$ kJ/g.

Although computation of heat of detonation by thermochemical codes such as the CHEETAH [1] have a stronger theoretical basis for prediction detonation properties than that proposed here, in spite of their complexities, they also require both density and heats of formation as input.

4. Conclusions

Reliable predictions of detonation parameters are a continuing need in the field of energetic materials. In this paper a simple approach is introduced for calculating the heat of detonation of explosives without using detonation products and experimental heat of formation, which are usually needed by computational or empirical methods. The methodology presented here have several advantages: (a) neither experimental condensed heats of formation nor densities need to be measured or estimated for calculating heat of detonation; (b) there is no need to estimate detonation products which are usually required for computer codes and empirical methods; (c) the correlations are much simple for rapid desk calculation of heat of detonation with about the same reliance on their answers as one could attach to complicated computer programs; (d) estimated gas phase heats of formation, which can be found easily by using additivity rules, rather than experimental condensed heats are used for calculation heat of detonation.

In brief, the new correlations were introduced here for simply hand calculating heat of detonation that require only the explosive's composition and estimated gas phase heats of formation based on group additivity methods. The new method is also simple in form and easy to use in a practical sense.

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