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Journal of Hazardous Materials 142 (2007) 54–57

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Determining heats of detonation of non-aromatic energetic compounds without considering their heats of formation

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Received 20 June 2006; received in revised form 22 July 2006; accepted 26 July 2006
Available online 31 July 2006

Abstract

A new procedure is introduced for calculating heats of detonation of non-aromatic energetic compounds through ratios of oxygen to carbon and hydrogen to oxygen as well as the contribution of some structural parameters. There is no need to use heats of formation of non-aromatic energetic compounds that are usually needed by the other methods. Moreover, this much simple method does not use any experimental and computed data of energetic materials. Predicted heats of detonation for 28 non-aromatic energetic compounds have a root mean square (rms) of deviation of 0.54 kJ/g from experiment, which show good agreement with respect to measured values. The new method is the simplest procedure for predicting heats of detonation and provides reliable results which are comparable with the other methods.

Keywords: Performance; Heat of detonation; Heat of formation; Correlation; Non-aromatic energetic compounds

1. Introduction

Detonation parameters such as detonation velocity, pressure and temperature can be determined by computer codes or empirical methods. A complicated computer code, e.g. CHEETAH [1], can be applied for explosives when their heats of formation and densities are known and the equations of state such as Becker–Kistiakosky–Wilson (BKW) [2] for the detonation products are assumed. Various empirical methods have been used to complete the computer output for desk calculations of factors related to various aspect of energetic materials [3]. As representative example, different procedures have been recently introduced for simple evaluation of detonation velocity of explosives using heat of detonation at loading density greater than 1 g/cm^3 [4,5] or any loading density [6], approximate detonation temperature [7], gas phase heat of formation [8] and structural parameters [9].

Detonation energy or heat of detonation has been regarded as one of the principal measures of performance of detonating explosives for many years. It 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. It can be determined from heats of formation of the reactants and the products of detonation through the relation [4]:

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

The condensed phase heat of formation of the explosive and the standard heats of formation of detonation products can be use to predict the heat of detonation of an energetic material. To obtain a greater release of energy upon detonation and an improvement in performance, a positive heat of formation (per unit weight) is favorable for an energetic compound.

The calculated heats of detonation can also be used to determine detonation pressure and velocity of explosives [10,11]. However, predicting fairly accurate heats of detonation, by simple empirical methods, are highly desired for calculating the various detonation parameters of energetic compounds. Moreover, their calculated values are useful in comparing the relative heat releasing of one explosive with another. The purpose of this work was to obtain the simplest method for estimating heats of detonation of non-aromatic energetic compounds without using their heats of formation. This work assumes that heat of detonation can be related to some structural parameters of explosive. There is no need to estimate the composition of detonation products and their thermochemical properties. The results will be

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doi:10.1016/j.jhazmat.2006.07.057

also compared with two empirical methods for 28 non-aromatic energetic compounds. The new method is also simple in form and easy to use in a practical sense.

2. New procedure for predicting heats of detonation of non-aromatic energetic compounds

Heat of detonation is an important detonation parameter which can be used as the energy available to do mechanical work and estimating potential damage to surroundings [12]. The Kamlet and Jacobs [4] introduced N_2, H_2O, CO_2 (but not CO) as the important products of decomposition reaction for calculating heat of detonation through Eq. (1). Rice and Hare [12] also used the predicted product concentrations by the CHEETAH 2.0/JCZS for computing heat of detonation using quantum mechanical calculations. Since thermochemical calculations show CO is a major component of gaseous products, their results by two sets of decomposition gases proposed by Kamlet and Jacobs and by the CHEETAH 2.0/JCZS confirmed that it would be needed to count CO as major product. The calculated heats of detonation by using quantum chemistry codes such as GAUSSIAN 98 [13] in addition to their complexities have some difficulties such as time and computer limitations. Using reliable detonation products, which counted the other detonation products such as CO and H_2 for oxygen lean explosives, give better predicted heats of detonation than those obtained by Kamlet and Jacobs procedure [10]. The calculated heats of detonation by Eq. (1) require measured or reliable estimation condensed phase heat of formation of explosives, such as those have been introduced for some classes of energetic materials [14–16]. It is shown recently that heat of detonation can be correlated with the explosive's elemental composition and simply estimated gas phase heat of formation of the explosive [17].

One can express heat of detonation as a function of basic parameters such as the elemental composition, oxygen balance and heat of formation. To express heats of detonation as a function of suitable structural parameters, various situations were studied and optimized with experimental data. The study of heats of detonation on various energetic compounds shows that one can possible to correlate heat of detonation with some structural parameters. Since difference of heats of formation for different isomers of energetic compounds are usually low [15,16], their heats of detonation are close to each other. The results show that the ratios of oxygen to carbon and hydrogen to oxygen as well as contributions of some structural parameters have important effects on the values of heats of detonation of non-aromatic energetic compounds. The ratios of oxygen to carbon and hydrogen to oxygen can determine relative amounts of different decomposition products which affect the amount heat of detonation according to Eq. (1). To establish a good correlation between molecular properties and measured data, finding reliable data would be needed. However, it is found that the following equation can provide the suitable pathway to obtain prediction of heat of detonation:

$$Q = y_1 + y_2 r_{O/C} + y_3 r_{H/O} + y_4 C_{SSP} \quad (2)$$

where y_1 to y_4 are adjustable parameters, $r_{O/C}$ and $r_{H/O}$ are the ratios of oxygen to carbon and hydrogen to oxygen respectively and C_{SSP} is the contribution of some specific structural parameters in non-aromatic $C_aH_bN_cO_d$ energetic compounds. Experimental data of various pure non-aromatic energetic compounds, which are listed in Table 1, were used to find adjustable parameters. Final correlation can be given as follows:

$$Q\,(\mathrm{kJ\,g^{-1}}) = 5.081 + 0.836 r_{O/C} - 1.604 r_{H/O} + 2.727 C_{SSP} \quad (3)$$

To use this correlation, C_{SSP} can be determined as follows:

(a) $C_{SSP} = 0.35$ for cyclic nitramine energetic compounds.
(b) C_{SSP} has the value -1 for an energetic compound which has –N–C(=O)–N– structural parameter, if it does not contain more than two nitro groups.

R-squared value or the coefficient of determination of this correlation is 0.93 [18]. As seen in Table 1, heats of detonation of 28 non-aromatic energetic compounds are calculated and compared with the experimental values. Deviation of measured values from calculated values, e.g. Dev = measured-predicted, are given in Table 1. Since different experimental data for heats of donation of some explosives are reported in literature, e.g. 6.32 kJ/g [19–21] and 6.08 kJ/g [22] for cyclotrimethylene trinitramine, the recent collected data of reference [21] were used in Table 1. The results are in good agreement with the values obtained from new method. The correlations can be applied to the oxygen lean as well as oxygen rich explosives. As seen, Eq. (3) requires no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties of explosive and assumed detonation products. Calculated heats of detonation are also compared with corresponding two empirical methods, namely Kamlet–Jacobs (K–J) [4] and Keshavarz–Pouretedal (K–P) [10]. The K–J and K–P methods assume that the heat of detonation of an energetic material 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. However, two empirical K–P and K–J methods require knowledge of measured or estimated condensed heat of formation of explosive. As shown in Table 1, the rms results of the new method is close to K–P method and is much lower than K–J procedure. The new method, which is based on only some structural, shows surprisingly very good agreement with experimental values as compared to K–J and K–P methods which need at least measured or reliable condensed phase heat of formation of energetic compounds. Thus, this may be taken as appropriate validation tests of the new method with $C_aH_bN_cO_d$ energetic materials. The study has shown that aromatic energetic compounds have different behavior, the same as previous work [17], because aromaticity. However, heats of detonation for aromatic energetic compounds without considering their heats of formation will be studied in future.

One important aspect of the present work is that it provides the easiest method for quick estimation of heats of detonation for a wide range of energetic materials including under-

Table 1
Comparison of calculated heats of detonation of Eq. (3) with K–J [4] and K–P [10] methods as well as measured values [21]

Energetic compound	Molecular formula	Q_{exp} (kJ/g)	Q_{new} (kJ/g)	Dev_{new}	Q_{KJ} (kJ/g)	Dev_{KJ}	Q_{KP} (kJ/g)	Dev_{KP}
Cyclotetramethylene tetranitramine	$C_4H_8N_8O_8$	6.197	6.10	0.09	6.78	−0.58	5.61	0.59
Cyclotrimethylene trinitramine	$C_3H_6N_6O_6$	6.322	6.10	0.22	6.82	−0.50	5.66	0.66
1,3,3-Trinitroazetidine	$C_3H_4N_4O_6$	6.343	6.64	−0.30	7.27	−0.93	6.37	−0.03
Hexanitrohexaazaisowurtzitane	$C_6H_6N_{12}O_{12}$	6.314	6.91	−0.59	6.86	−0.55	6.27	0.04
Pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	6.322	6.02	0.30	6.89	−0.57	6.35	−0.03
Methyl nitrate	CH_3NO_3	6.748	5.98	0.76	7.38	−0.63	6.82	−0.07
Nitroethane	$C_2H_5NO_2$	1.686	1.91	−0.22	6.43	−4.74	1.16	0.53
Nitroglycerine	$C_3H_5N_3O_9$	6.671	6.70	−0.03	7.15	−0.48	6.72	−0.05
Nitroguanidine	$CH_4N_4O_2$	3.071	3.54	−0.47	4.61	−1.54	2.92	0.15
Bi-trinitroethylurea	$C_5H_6N_8O_{13}$	6.454	6.51	−0.06	6.49	−0.04	6.49	−0.04
Diethyleneglycol dinitrate	$C_4H_8N_2O_7$	4.566	4.71	−0.14	6.62	−2.05	4.40	0.17
Dioxyethylnitramine dinitrate	$C_4H_8N_4O_8$	5.458	5.15	0.31	6.9	−1.44	5.46	0.00
Dipentaerythritol hexanitrate	$C_{10}H_{16}N_6O_{19}$	5.143	5.32	−0.18	6.63	−1.49	5.15	−0.01
Ethriol trinitrate	$C_6H_{11}N_3O_9$	4.244	4.37	−0.13	6.62	−2.38	3.87	0.37
Ethylene dinitramine	$C_2H_6N_4O_4$	4.699	4.35	0.35	6.34	−1.64	4.60	0.10
Ethyl nitrate	$C_2H_5NO_3$	4.154	3.66	0.49	6.85	−2.70	3.48	0.67
Manitol hexanitrate	$C_6H_8N_6O_{18}$	6.384	6.88	−0.49	7.22	−0.84	6.35	0.03
Nitromethane	CH_3NO_2	4.821	4.35	0.47	6.79	−1.97	4.65	0.17
Pentaerytritol trinitrate	$C_5H_9N_3O_{10}$	5.230	5.31	−0.08	6.67	−1.44	5.24	−0.01
Triethyleneglycol dinitrate	$C_6H_{12}N_2O_8$	3.317	3.79	−0.47	6.17	−2.85	2.53	0.79
Metriol trinitrate	$C_5H_9N_3O_9$	4.945	4.98	−0.04	6.85	−1.91	4.99	−0.04
Nitroethylpropanediol dinitrate	$C_5H_9N_3O_8$	4.340	4.61	−0.27	6.73	−2.39	4.36	−0.02
Erythritol tetranitrate	$C_4H_6N_4O_{12}$	6.356	6.79	−0.43	7.17	−0.81	6.52	−0.16
Nitromethylpropanediol dinitrate	$C_4H_7N_3O_8$	5.295	5.35	−0.05	6.93	−1.64	4.45	0.85
Polyvinyl nitrate	$C_2H_3NO_3$	4.781	4.73	0.05	6.98	−2.20	4.54	0.24
Butanetriol trinitrate	$C_4H_7N_3O_9$	6.022	5.71	0.31	6.96	−0.94	6.06	−0.04
Nitrourea	$CH_3N_3O_3$	3.745	3.26	0.49	4.21	−0.47	3.79	−0.04
Urea nitrate	$CH_5N_3O_4$	3.211	3.69	−0.48	3.64	−0.43	3.29	−0.08
rms deviation (kJ/g)				0.54		1.20		0.46

oxidized and over-oxidized non-aromatic explosives. The new method can be applied for any new $C_aH_bN_cO_d$ non-aromatic energetic compounds. As representative example, 3-nitro-1,2,4-triazole-5-one (NTO) has measured condensed heat of formation −14.3 kcal/mol [12] and heat of detonation 3.148 kJ/g [21]. It has explosive performance characteristics similar to RDX but less sensitive than RDX because it is able to withstand much mechanical and thermal shock without igniting [23]. However, the attractive attributes can make it as a good candidate for a variety defense and civilian applications [23]. The calculated heats of detonation of NTO are 2.54 (Dev = 0.61) kJ/g, 4.77 (Dev = −1.62) kJ/g and 3.44 (Dev = −0.29) kJ/g for the new, K–J and K–P methods, respectively.

3. Conclusions

The effectiveness of an energetic compound depends on the amount of energy available in it and the rate of release of available energy when decomposition occurs. It is proposed here that the heat of detonation as one of the important detonation parameters can most appropriately be expressed as ratio of oxygen to carbon, ratio of hydrogen to oxygen and some structural parameters.

There is a continuing need to obtain better theoretical models of behavior of energetic materials and an improved diagnostic capability to measure the complex chemical and hydrodynamic process during detonation. Since the values of condensed heat of formation are hardly known experimentally for new energetic materials of interest which are usually needed for available methods, the present procedure can be used to estimate their heat of detonation without any difficulties.

Though heat of detonation may be measured experimentally or calculated from theory, in this paper a simple approach is introduced for calculating heat of detonation of energetic materials without using detonation products and heat of formation. The methodology presented here provides a new correlation which is 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 or empirical methods which need at least heats of formation of energetic materials.

Acknowledgements

I would like to thank the research committee of Malek-ashtar University of Technology (MUT) for supporting this work. This research was supported in part by Institute of Chemical and Science Technology-Tehran-Iran Research Council Grant (No. ICST-8I03-2138).

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