Approximate prediction of melting point of nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds

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Abstract

A simple new procedure is introduced to predict melting point of selected class of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics energetic compounds. The number of nitrogen and oxygen as well as the number of nitramine group and the contribution of some specific functional groups would be needed in the new method. Energetic compounds should contain at least one of the functional groups including $N-NO_2$, $C-ONO_2$ or nonaromatic $C-NO_2$. Calculated melting point for 33 nitramines, nitrate esters, nitrate salt and nitroaliphatics are compared with experimental data. Predicted melting points have average deviation of 5.4% for these energetic compounds.
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1. Introduction

Determination of performance and physical properties of a new energetic compound are very important to chemist and energetic material user. The performance of new energetic materials can be evaluated by thermochemical computer codes such as CHEETAH [1]. Moreover, various empirical methods exist so that they complemented the computer output related to detonation performance [2]. Some new simple methods have been recently introduced for simple evaluation thermochemical and important properties of energetic compounds, which contain detonation temperature [3–5], heat of detonation [6,7], Gurney velocity [8], specific impulse [9,10], impact sensitivity [11,12] and heat of formation [13–15].

To estimate the properties of organic compounds, group-contribution methods such as those given by Joback and Reid [16], Lydersen [17], Ambrose [18], Klincewicz and Reid [19], Lyman et al. [20], and Horvath [21] can be used. The property of a compound is a function of structurally dependent parameters in these methods, which are determined by summing the frequency of contribution of each group occurring in the molecule. Many of these methods are of questionable accuracy and limited applicability for organic energetic compounds.

In contrast to the other physicochemical properties, melting points are not very well estimated by the group contribution method [22–24]. Moreover, there is no reliable method for predicting melting points of energetic compounds. The paper presents a new simple scheme for obtaining some important classes of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics materials. The main intent was to investigate the likelihood of obtaining a simple procedure for calculating fusion temperature of mentioned energetic materials. To show the reliability of predicted melting points, the results for 33 well-known and two new energetic compounds are compared with the measured data. The introduced correlation will be very valuable in directing research efforts towards design of energetic organic molecules with desired melting point.

2. Development of new method

The group-contribution method for the estimation method of physical properties of pure compounds proposed by Joback and Reid [25] is popular among the other group-contribution methods. The melting points T_m of pure organic compounds estimated from the Joback and Reid method can be expressed by

$$T_m \text{ (K)} = 122.5 + \sum N_i C_{mi} \tag{1}$$

where N_i is the number of groups of type i and C_{mi} is the group contributions of the melting points resulting from the
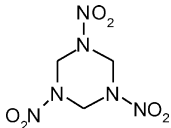

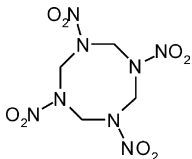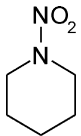* Tel.: +98 312 522 5071; fax: +98 312 522 5068.
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group *i* of the molecule. Although some developments such as method of Xu and Yang [26,27] were used for estimating boiling and melting points of organic compounds, no reliable methods are now available to estimate freezing point of organic compounds. One may use group-contribution methods for a very approximate guess.

Since there are no available methods for obtaining melting point of different classes of energetic materials, one can use a new scheme to derive useful equation for some classes of energetic materials. The study of melting point for various some important classes of energetic compounds containing nitramines, nitrate esters, nitrate salts and nitroaliphatics materials shows that it is possible to express their melting point as a function of elemental composition as well as some special structural parameters and functional groups. To investigate the important structural factors, experimental data of various $C_aH_bN_cO_d$ nitramines, nitrate esters, nitrate salts and nitroaliphatics, which are listed in Table 1, were used. The results show that the follow-

Table 1
Comparison of predicted melting point (K) of nitramines, nitrate esters, nitrated salts and nitroaliphatics energetic compounds with the experimental data

No.	Energetic compound	Experiment[a]	New method	%Dev
1	$CH_3CH_2ONO_2$	178.6	187.65	5.1
2	$CH_3CH(ONO_2)CH_3$	190.81	187.65	−1.7
3	CH_3ONO_2	190.81	187.65	−1.7
4	$O_2NOCH_2CH_2CH_2CH_2ONO_2$	285	257.86	−9.5
5	$O_2NOCH_2CH_2CH_2CH_2CH_2ONO_2$	256.6	257.86	0.5
6	$CH_3CH(ONO_2)CH_2CH_2ONO_2$	253.4	257.86	1.8
7	$CH_3CH(ONO_2)CH_2CH(ONO_2)CH_3$	254.7	257.86	1.2
8	$O_2NOCH_2CH(ONO_2)CH_2ONO_2$	286	293.73	2.7
9	$(O_2NOCH_2)_4C$	413	398.29	−3.6
10	$CH_3(C=O)NH_3NO_3$	361	380.03	5.3
11	$(C_6H_5)_4NNO_3$	387.2	355.25	−8.3
12	$[CH_3(CH_2)_6]_4NNO_3$	345	355.25	3.0
13	$[CH_3(CH_2)_3]_4NNO_3$	392.2	355.25	−9.4
14	$[CH_3(CH_2)_5]_4NNO_3$	345	355.25	3.0
15		478.5	472.80	−1.2
16		548	556.91	1.6
17	$(CH_3)_2NNO_2$	345.45	304.58	−11.8
18		267.65	304.58	13.8
19	$C_6H_5NHNO_2$	319.15	304.58	−4.6
20	$CH_3C(CH_2OH)_2NO_2$	424	418.50	−1.3
21	$(O_2N)_3CC(NO_2)_3$	420	424.38	1.0
22	$HOCH_2C(CH_3)_2NO_2$	361.7	393.72	8.9
23	$(O_2N)_3CH$	292	253.74	−13.1
24	$(CH_3)_3CNO_2$	298.65	300.25	0.5
25	$(CH_3)_2C(NO_2)_2$	326	311.34	−4.5
26	$O_2NCH_2CH_2NO_2$	251.8	242.65	−3.6
27	CH_3NO_2	244.6	231.56	−5.3
28	$(CH_3)_2CHCH_2NO_2$	196.3	197.21	0.5
29	$CH_3CH_2CH_2NO_2$	169.16	197.21	16.6
30	$CH_3CH_2CH_2NO_2$	183.63	197.21	7.4
31	$CH_3CH_2CH_2CH_2NO_2$	191.82	197.21	2.8
32	$(CH_3)_2CHNO_2$	181.83	197.21	8.5
33	$C(NO_2)_4$	287.05	333.52	16.2
Average deviation				5.4

[a] Experimental data taken from NIST Chemistry Web Book [29] so that references for individual molecules are given therein.

ing general equation with some adjustable coefficients is suitable for this purpose:

$$T_m \text{ (K)} = z_1 + z_2 c + z_3 d + z_4 C_{SFG} + z_5 n_{N-NO_2} \qquad (2)$$

where C_{SFG} is the contribution of specific functional groups, n_{N-NO_2} the number of nitramine group in the energetic compound, z_1 to z_5 are adjustable parameters. Experimental data given in Table 1 were used to optimize the values of z_1 to z_5. The results give the following optimized correlation:

$$T_m \text{ (K)} = 220.47 + 30.220c + 24.780d$$
$$- 68.691 C_{SFG} - 25.891 n_{N-NO_2} \qquad (3)$$

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

(a) $C_{SFG} = 0$ for nitrated salt.
(b) C_{SFG} has the values 2.0, 2.5 and 3.5 for nitrated energetic compounds which have one, two and three or four –O–NO$_2$ groups, respectively.
(c) $C_{SFG} = -1.0$ for nitro or nitrated energetic compounds that have at least one –OH functional groups.
(d) $C_{SFG} = n_{NO_2} - 1$ for nitro compounds in which carbon attached to nitro groups do not contain hydrogen. The n_{NO_2} is the number of nitro groups.
(e) $C_{SFG} = 1.5$ for mono nitro compounds in which the compound has general formula R'CH–RCH–NO$_2$ (R or R' = –H, alkyl).

R^2 value or the coefficient of determination of this correlation is 0.951 [28]. As seen in Table 1, melting point of 33 nitramines, nitrate esters, nitrate salts and nitroaliphatics materials are calculated and compared with the experimental values. The percent error [(predicted − measured)/measured] × 100, are given in Table 1. The results are in good agreement with values obtained from mentioned methods. The latest reported values of the NIST Chemistry Web Book [29] were taken for comparison the mentioned method with experimental data because there are different reported values from different sources, e.g. 244.6, 244.55, 243.11, 244 and 243.95 K are several different reported experimental data for nitromethane.

As indicated in Table 1, the average percent of deviation for new approach is 5.4%. The estimated melting point by new correlation is within 5.0% of the reported values for 19 energetic materials, within 5–10% for nine materials, and more than 10% for remainder five energetic compounds.

The new method can be applied for any new $C_a H_b N_c O_d$ nitramines, nitrate esters, nitated salts and nitroaliphatics energetic compounds. As two representative examples, 1,3,3-trinitroazitidine (TNAZ) and 1,1,3,3-tetranitrocyclobutane (TNCB) are two new organic explosives. Archibald and coworkers synthesized TNAZ at first in 1990 [30]. It has a melting point of 377 K. Archibald et al. [31] used oxidative nitration of 1,3-dinitrocyclobutane with AgNO$_3$ and NaNO$_2$ to synthesize TNCB. It also has a melting point of 438 K. The calculated melting points by Eq. (3) for two new explosives TNAZ and TNCB are 395 and 401 K, respectively. Thus, percent of deviation for TNAZ and TNCB are 4.9 and −8.2% respectively.

3. Conclusions

Physical properties of an energetic compound are the essential parameters of somewhat more practical importance to the explosive user. The present method can act as predictive tools for estimating melting point of organic nitramines, nitrate esters, nitrated salts and nitroaliphatics. Since the present method requires as input only some structural parameters of energetic compounds, it may be appealing and the results are very promising. Comparison of calculated results with experimental data listed in Table 1 may be taken as appropriate validation of the new procedure for use with nitramines, nitrate esters, nitrated salts and nitroaliphatics energetic compounds. The new method provides the simplest procedure for hand calculation of melting point of energetic compounds.

Acknowledgements

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