Predicting activation energy of thermolysis of polynitro arenes through molecular structure

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A R T I C L E   I N F O

A B S T R A C T

The paper presents a new method for activation energy or the Arrhenius parameter E_a of the thermolysis in the condensed state for different polynitro arenes as an important class of energetic molecules. The methodology assumes that E_a of a polynitro arene with general formula $C_aH_bN_cO_d$ can be expressed as a function of optimized elemental composition as well as the contribution of specific molecular structural parameters. The new method can predict E_a of the thermolysis under conditions of Soviet Manometric Method (SMM), which can be related to the other convenient methods. The new correlation has the root mean square (rms) and the average deviations of 13.79 and 11.94 kJ/mol, respectively, for 20 polynitro arenes with different molecular structures. The proposed new method can also be used to predict E_a of three polynitro arenes, i.e. 2,2′,2″,4,4′,4″,6,6′,6″-nonanitro-1,1′:3′,1″-terphenyl (NONA), 3,3′-diamino-2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl-3,3′-diamine (DIPAM) and *N,N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA), which have complex molecular structures.

1. Introduction

Quantum mechanical and empirical methods can help the chemists to improve systematic and scientific formulation of appropriate futuristic target molecules having enhanced performance as well as good thermal stability, impact and friction sensitivity. Due to the expenditure connected with the development and synthesis of a new energetic material, different theoretical approaches can be used to determine performance and physicochemical properties of energetic compounds before their synthesis [1–3].

Many kinds of sensitivities such as heat, friction, impact, shock and electrostatic charges have been identified in terms of nature of stimuli causing detonation. As representative examples, some theoretical methods have been introduced to determine impact and shock sensitivity of different classes of energetic materials [4–27].

Stability of polynitro compounds is necessary to avoid undesirable decomposition or self-initiation during their handling, storing and the application itself. Prediction of thermal stability on mentioned compounds is an important starting point to evaluate the stability. The experimental data for thermal reactivity can be obtained by various methods of thermal analysis and

gasometry or by a variety of methods based on thermal explosion. The purpose of this work is to present a new approach for obtaining activation energy of thermolysis (E_a) of $C_aH_bN_cO_d$ polynitro arenes as an important class of organic energetic materials. It will be shown that how elemental composition and two structural parameters can be used to obtain a novel general correlation. Predicted results for 20 polynitro arenes will be compared with corresponding measured data. The method will also be applied to three polynitro arenes, i.e. 2,2′,2″,4,4′,4″,6,6′,6″-nonanitro-1,1′:3′,1″-terphenyl (NONA), 3,3′-diamino-2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl-3,3′-diamine (DIPAM) and *N,N*-bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline (NTFA), of which molecular structures are given in Fig. 1.

2. Theory

2.1. The basic data source for activation energy of thermolysis

The knowledge of the thermal stability of polynitro compounds in the condensed state is the most significant from the point of view of technological practice. The isothermal manometric method with a glass compensating manometer of the Bourdon type, which can be called Soviet Manometric Method (SMM), is one of the important methods to examine the kinetics of thermolysis of energetic materials in vacuum. The data obtained by this method is the basic data on the Arrhenius parameters of non-autocatalyzed
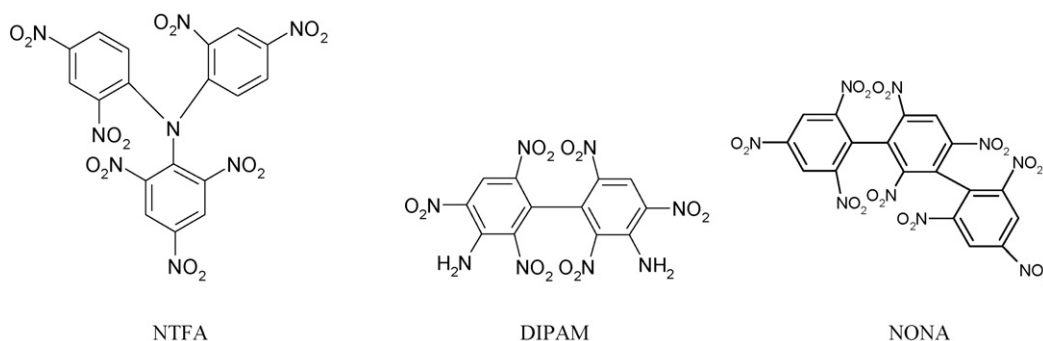
Fig. 1. Molecular structures of NTFA, DIPAM and NONA.

thermal decomposition of polynitro arenes [28]. It was found that the results of some methods of the differential scanning calorimetry (DSC) are directly comparable with the results of SMM [29,30]. If a relationship, such as a calibration curve, exists between the results of the differential thermal analysis and thermogravimetric analysis with the results of the SMM, the results of mentioned methods can be converted to SMM data [31–33]. The data obtained by SMM are known to correspond to the primary non-autocatalyzed stage of thermal decomposition of energetic compounds [28,29,34]. However, more accurate and reliable data source on the activation energies of the non-autocatalyzed thermal decomposition in the condensed state of polynitro arenes studied in the present paper are on the basis of SMM because the discrepancy in principles and physical conditions prevents a uniform classification of a large majority of results obtained in various laboratories. The existing literature also lacks a more complete survey of the published E_a of the monomolecular non-autocatalyzed thermal decompositions of mentioned compounds in the condensed state classified according to the primary thermolytic fissions [28]. Moreover, SMM uses the respective measurement in vacuum and isothermal conditions which can minimize the effects of consecutive reactions of intermediates and products of thermal decomposition both with each other and with the starting energetic material [34].

2.2. New aspects of thermolysis of polynitro compounds

Zeman and co-workers have performed some studies on different classes of polynitro compounds to attribute the Arrhenius parameters of low temperature decomposition to some specific parameters of different compounds. Zeman [35] used the ^{15}N NMR chemical shifts of nitramines to present the relationship between activation energies of this decomposition and the aforesaid chemical shifts of nitrogen atoms in the most reactive nitro groups. Since the abilities of nitramine groupings participation in primary initiation processes are different, Zeman and Friedl [36] have demonstrated thermal reactivity in terms of the electronic charges at nitrogen atoms of the nitramines calculated on the basis of the Mulliken population analysis of electron densities obtained by ab initio DFT B3LYP/6-31G** method. Zeman et al. [29,34,35,37–39] have shown that the activation energies for thermal decomposition of selected groups of polynitro arenes, polynitro azaarenes, nitro paraffins, nitramines, nitrosamines, nitrate esters and primers can be related to the respective heats of detonation through a modified Evans–Polanyi–Semenov (EPS) equation. The heats of detonation used in EPS equation were calculated for monocrystals by means of semi-empirical relationships devised by Pepekin et al. [40]. Zeman and co-workers [41–43] have tried to derive a linear relationship between oxygen balance of nitramines, nitrosamines, nitroesters, polynitroparaffins to activation energy of thermolysis of these compounds. Their linear relation has satisfied for selected groups of

mentioned energetic compounds. Since Kamlet and Adolph [9,10] have found the existence of a correlation between impact sensitivity and oxygen balance of different classes of energetic compounds, it may be concluded that there is a direct relationship between impact sensitivity and the activation energy of non-autocatalyzed thermolysis for selected groups of different classes of explosives.

Due to the existence of various factors affecting the experimental data of activation energies for different classes of energetic compounds [29], no general correlations have been developed to predict E_a for specified classes of explosives.

3. Results and discussion

The study of the activation energies for thermal decomposition of various polynitro arenes has shown that it is possible to derive a general novel correlation for predicting activation energy of these compounds. The results have shown that elemental composition and two structural parameters are important for a $C_aH_bN_cO_d$ energetic polynitro arene. Molecular structures of some polynitro arenes and corresponding measured E_a on the basis of SMM are given in Table 1

. The first structural parameter is either the number of $-NH(C=O)-C(=O)NH-$ groups (e.g. HNO) or amino groups so that more than one $-NH_2$ groups should be attached to aromatic rings (e.g. DATB), which can increase the value of E_a. The existence of either one α-CH (e.g. TNT) or methoxy group attached to one aromatic ring in form α-CH or $CH_3O-[C(NO_2)-CH-C(NO_2)]$ is the other important structural parameter in predicting activation energy, which has an opposite effect with respect to the first structural parameter. Since elemental composition can be used to determine impact and shock sensitivity of aromatic compounds [4,5,8–10], the study of activation energy for polynitro arenes has shown that this parameter is also important here. It was found that the number of amino groups can affect the sensitivity and performance of nitroaromatic compounds [8,44,45]. However, the effect of amino groups in predicting activation energy becomes appreciable when more than one amino group attached to aromatic rings. Since polynitroaromatics with α-CH are one class of energetic materials that have different impact sensitivity correlation [4], however, the presence of one α-CH or $CH_3O-[C(NO_2)-CH-C(NO_2)]$ in the molecular structure of polynitro arenes can influence the value of E_a. To predict activation energy of $C_aH_bN_cO_d$ energetic polynitro arenes as a function of mentioned parameters, the following equation can be used:

$$\log(E_a) = z_1 + z_2 OEC + z_3 n_{NHCOCONH, NH_2 > 1}$$
$$+ z_4 E_{\alpha\text{-CH or } CH_3O-[C(NO_2)-CH-C(NO_2)]} \quad (1)$$

where OEC, $n_{NHCOCONH, NH_2 > 1}$ and $E_{\alpha\text{-CH or } CH_3O-[C(NO_2)-CH-C(NO_2)]}$ are the contribution of elemental composition, the first and the

Table 1
Comparison of the results of new method for calculations of activation energy (kJ/mol) of polynitro arenes with experimental data [34]
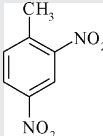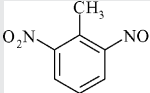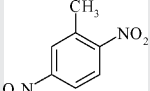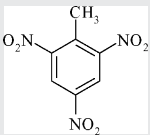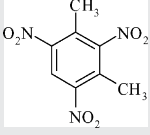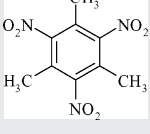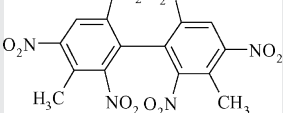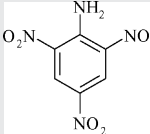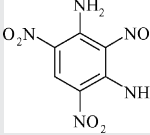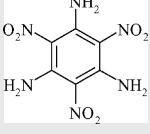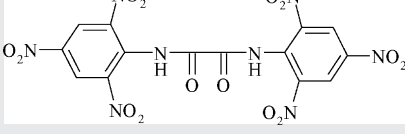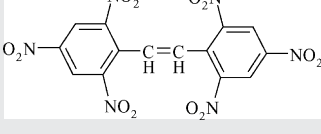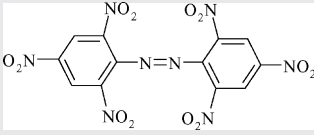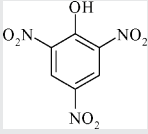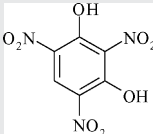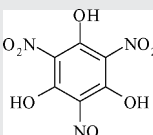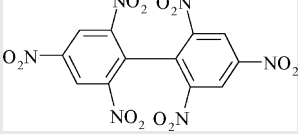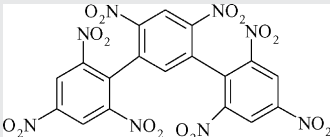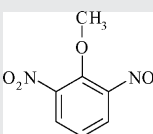
Chemical name	Molecular structure	$(E_a)_{exp}$	$(E_a)_{cal}$	Deviation
2,4-Dinitrotoluene (2,4-DNT)		139.56	152.27	−12.71
2,6-Dinitrotoluene (2,6-DNT)		198.87	202.59	−3.72
3,5-Dinitrotoluene (3,5-DNT)		186.08	202.59	−16.51
2,4,6-Trinitrotoluene (TNT)		144.44	122.25	22.19
2,4-Dimethyl-1,3,5-trinitrobenzene (TNX)		146.95	159.89	−12.94
2,4,6-Trimethyl-1,3,5-trinitrobenzene (TNMs)		185.08	157.19	27.89
3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitro-1,1′-biphenyl (DMHNB)		129.90	140.68	−10.78
2,4,6-Trinitroaniline (PAM)		129.79	123.29	6.50
2,4,6-Trinitrobenzene-1,3-diamine (DATB)		196.80	179.98	16.82
2,4,6-Trinitrobenzene-1,3,5-triamine (TATB)		175.00	187.71	−12.71
N,N′-Bis(2,4,6-trinitrophenyl)oxamide (HNO)		215.62	197.20	18.42
(E)-2,2′,4,4′,6,6′-Hexanitrosilbene (HNS)		183.80	177.01	6.79

Table 1 (*Continued*)

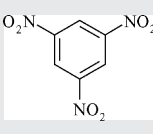| Chemical name	Molecular structure	$(E_a)_{exp}$	$(E_a)_{cal}$	Deviation
(*E*)-Bis(2,4,6-trinitrophenyl)diazene (HNAB)		121.83	135.32	−13.49
2,4,6-Trinitrophenol (PA)		161.18	153.09	8.09
2,4,6-Trinitrobenzene-1,3-diol (TNR)		144.88	141.66	3.22
2,4,6-Trinitrobenzene-1,3,5-triol (TNPg)		114.64	131.09	−16.45
1,3,5-Trinitrobenzene (TNB)		180.03	165.45	14.58
2,2′,4,4′,6,6′-Hexanitro-1,1′-biphenyl (HNB)		207.24	193.67	13.57
2,2′,2″,4,4′,6,6′,6″-Octanitro-1,1′:3′,1″-terphenyl (ONT)		281.58	282.39	−0.81
2,4,6-Trinitroanisole (TNA)		113.80	113.12	0.68
rms deviation (kJ/mol)				13.79

second structural parameters, respectively; z_1–z_4 are adjustable parameters which can be found from experimental data given in Table 1. OEC is the optimized elemental composition of polynitro arenes with general formula $C_aH_bN_cO_d$ which can be obtained by suitable combinations of *a*, *b*, *c* and *d*. To find OEC and adjustable parameters, multiple linear regression method [46] was used. Since the equation set is overdetermined [46], the left-division method for solving linear equations uses the least squares method. The value of OEC was found as OEC = $2.74a − 1.48b + 2.31c − d$. The optimized correlation can be expressed as follows:

$$\log(E_a) = 2.25 + 0.0337\text{OEC} + 0.146n_{\text{NHCOCONH,NH}_2>1}$$

$$+0.124E_{\alpha\text{-CH or CH}_3\text{O}-[\text{C(NO}_2)-\text{CH}-\text{C(NO}_2)]} \qquad (2)$$

Since the existence of a variety of different factors can influence the activation energy [28], *R*-squared values or the coefficients of

determination of Eq. (2) is 0.87 [46]. Predicted results using the new method and experimental data of SMM procedure as well as deviations are given in Table 1. As indicated in Table 1, predicted activation energies for 20 polynitro arenes have a root mean square (rms) of deviation from experiment of 13.79 kJ/mol, which show the results of new method are in good agreement with experimental values. The average deviation in Table 1 for new approach is 11.94 kJ/mol. The estimated activation energy by new correlation is within 10 kJ/mol of the reported values for 7 energetic compounds, within 10–20 kJ/mol for 11 polynitro arenes, and more than 20 kJ/mol for remainder 2 energetic compounds.

The present method can be applied for heat resistant polynitro arenes. For example, NTFA, DIPAM and NONA are well-known high thermostable and technologically exploited explosives. NTFA is a well-known Russian thermostable explosive for downhole well applications [47]. DIPAM is extremely insensitive to electro-

static discharge, requiring more than 32 kJ for initiation [48,49]. It has been used to achieve stage separation in space rockets and for seismic experiments on the moon in a similar manner to HNS [48,49]. NONA has a good heat stability which together with a low volume of split-off gases renders it an interesting material for booster explosives in space technology [48,49]. The calculated activation energies by Eq. (2) for NTFA, DIPAM and NONA are 192.18, 210.68 and 226.72 kJ/mol, respectively. Predicted results are relatively close to the measured values of NTFA ($E_a = 187.00$ kJ/mol [50], deviation = -5.18 kJ/mol), DIPAM ($E_a = 190.23$ kJ/mol [28], deviation = -20.45 kJ/mol), NONA ($E_a = 214.11$ kJ/mol [50], deviation = -12.61 kJ/mol).

4. Conclusions

A novel simple method has been developed for prediction of activation energy of polynitro arenes. Only molecular structure without using any experimental data or computed values would be needed to calculate activation energy in this new method. The results given in Table 1 may be taken as an appropriate validation test of the new method. The new procedure exhibits an improved accuracy and simple applicability to an important class of energetic materials, namely polynitro arenes. The results of this work are appealing to chemists because the new model gives the simplest and easiest novel pathway to calculate activation energy of polynitro arenes.

Acknowledgement

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