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Prediction of decomposition onset temperature and heat of decomposition of organic peroxides using simple approaches

Narges Zohari[1] · Mohammad Hossein Keshavarz[2] · Zeinab Dalaei[1]

Abstract Decomposition onset temperature and heat of decomposition are two important parameters for assessment of thermal stability of an energetic compound. This study presents two new correlations for predicting decomposition onset temperature and heat of decomposition of organic peroxides through their molecular structures. For 33 organic peroxides with different molecular structures, the new model for decomposition onset temperature gives the root-mean-square (rms) and the average absolute (σ) deviations 6.06 and 5.18 °C, respectively. The values of rms and σ deviations for heat of decomposition are also 146.41 and 118.19 J g^{-1}, respectively. The proposed new models give good predictions for further eight organic peroxides containing complex molecular structures. The predicted results have also given more reliable results as compared to two of the best available methods, which are based on complex quantum mechanical parameters. High reliability of the new methods has been confirmed statistically by internal and external validation methods.

Introduction

Thermal stability of an organic compound containing energetic groups is an important feature for assessment of its sensitivity and shelf life [1–5]. Thermal analysis methods are frequently applied to estimate thermal stability of different types of energetic compounds [6–8]. They can be used to determine temperature [9], heat [10, 11] and activation energy [12] of decomposition process of energetic materials. Beside heat, the other kinds of stimuli such as impact [13–16], shock [17], friction [18] and electrostatic charges [19, 20] can also cause initiation reaction of energetic compounds. It was shown that activation energy of thermolysis of different classes of energetic compounds can be related to impact [21] electrostatic [22, 23] and friction [24] sensitivities.

Organic peroxides contain hazardous peroxide functional group in their molecular structures that can initiate their decomposition upon external stimuli such as impact [25]. They are unique in their stability characteristics and potential hazards because of the weak oxygen–oxygen bond in the peroxide functional group [26, 27]. However, they can decompose violently and produce free radicals by heat, friction, mechanical shock, low temperature and various contaminants [28–30]. Thus, decomposition of organic peroxides can cause dangerous occurrences. Due to the various incidents caused by organic peroxides in the laboratory or industrial processes during their storage and transportation, the recognition of their thermal stability has the utmost importance from safety point of view [31–36].

✉ Narges Zohari
nargeszohari@gmail.com

✉ Mohammad Hossein Keshavarz
keshavarz7@gmail.com; mhkeshavarz@mut-es.ac.ir

1 Faculty of Chemistry and Chemical Engineering, Malek-ashtar University of Technology, P.O. Box 15875-1774, Tehran, Islamic Republic of Iran

2 Department of Chemistry, Malek-ashtar University of Technology, P.O. Box 83145/115, Shahin-shahr, Isfahan, Islamic Republic of Iran

Therefore, the theoretical and practical studies of reactivity hazards of organic peroxides can help chemists and chemical engineers for the safe use of these compounds. It is necessary to investigate some related characteristics to thermodynamic and kinetic stability of organic peroxides such as decomposition onset temperature, heat of decomposition and self-accelerating decomposition temperature [37–40].

Organic peroxides are widely used in industrial and military fields such as oxidants, curing agent, polymerization catalyst and bleaching agent [27, 41]. There are several techniques for determining thermal stability hazards of organic peroxides, e.g., differential scanning calorimetry (DSC) and calorimetry [37–44]. The study of thermolysis of various energetic compounds can be used for estimation of their thermal stability and sensitivity parameters [21–23, 45–47]. Since thermal stability of hazardous materials is an important feature in their shelf life and safety aspects [9, 48, 49], several methods were reported recently for prediction of thermal stability of hazardous materials such as nitroaromatic energetic compounds, nitramines, nitroaliphatic energetic materials [46, 50–52], ionic liquids [53, 54] and organic peroxides [37–40].

The quantitative structure–property relationships (QSPR) method was applied to explore the relationship between the heat and temperature of decomposition of organic peroxides and their quantum properties [38, 40]. The QSPR method was also used to derive a correlation between self-accelerating decomposition temperature (SADT) of organic peroxides and their molecular structures [39] or their quantum mechanical properties [37]. Complex descriptors were used in these works, which include dissociation energy, bond length of the oxygen–oxygen bond, the number of peroxide functional groups, molecular hardness, the oxygen balance, the charge on oxygen atoms of peroxide bonds, the average local Fukui function on O atoms of the peroxide bond and the eV energy difference between the LUMO and HOMO orbitals [37–40]. All of these methods require specific computer codes and expert researchers.

The purpose of this work is to introduce two new simple models for evaluation of decomposition onset temperature and heat of decomposition as two important parameters for assessment of thermal stability of organic peroxides [2, 8, 55–68]. These models correlate decomposition onset temperature and heat of decomposition of organic peroxides to their molecular structures using several simple molecular descriptors. The predicted results by this new method are also compared with two of the best available methods, i.e., Lu et al. [38] and Prana et al. [40] models.
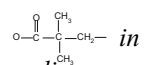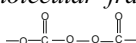
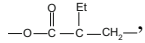## Theory

Onset decomposition temperature

The study of organic peroxides has indicated that it is possible to express decomposition onset temperature of these compounds as a function of several structural parameters. The data of decomposition onset temperature of 41 organic peroxides, which were obtained by DSC method [38, 40], were used for constructing and testing the new model. Experimental data of 33 different organic peroxides containing simple molecular structures have been used to derive the new model that is given in Table 1. Multiple linear regression method was used to obtain the relationship between decomposition onset temperature and molecular structure in Eq. (1) [69] as:

$$T_{\text{Dec}} = 165.81 - 4.92 n_{\text{O}} - 29.11 \lambda_{\text{C=O}} - 14.02 \lambda_{\text{sym}} - 30.81 \lambda' \tag{1}$$

where T_{Dec} is decomposition onset temperature in °C; n_{O} represents the number of oxygen in molecular formula; $\lambda_{\text{C=O}}$ is 1.0 for the presence of carbonyl group; and λ_{sym} is also 1.0 for those peroxides that have the same fragments attached to the –O–O– bond, i.e., R–O–O–R′ where R = R′. The presence of some molecular fragments may also affect the values of T_{Dec}, which are incorporated in λ' as correcting factor. Positive and negative contributions of various structural parameters in λ' are discussed in the following sections.

Positive values of λ

The presence of molecular fragments $\overset{\text{O}}{\underset{}{\text{O–C–C–CH}_2}}\text{–}$ in any organic peroxide or –O–C–O–C–O– in acyclic peroxides: The value of λ' is 1.0 for these peroxides.

The existence of molecular moieties $\text{–O–C–C–CH}_2\text{–}$, –C–O–O–C– or $\bigvee\hspace{-0.3em}\bigwedge$ as well as $\text{–C–CH}_2\text{–}$: For three initial molecular fragments, λ' is 0.7. Meanwhile, the value of λ' for the latest molecular moiety is given as: $\lambda' = 0.7\times$ the number of $\text{–C–CH}_2\text{–}$ in molecular structure of peroxide.

Negative values of λ

For those peroxides containing –O–C(R)(R′)–O– molecular fragment structure, where R and R′ can be –CH₃ or –CH₂–CO, or –C(CO)₂ in their molecular structures, the value of λ' is −1.0.

Heat of decomposition

The data of heat of decomposition of 41 organic peroxides, which were obtained by DSC method [38, 40], were also

Table 1 Comparison of the predicted decomposition onset temperature and heat of decomposition of some organic peroxides by Eqs. (1) and (2), Lu et al. [38] and Prana et al. [40] with experimental data as training test

No.	Name	T_d (exp)/°C	T_d (cal)/°C	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.	ΔH (exp)/ J g^{-1}	ΔH (cal)/ J g^{-1}	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.
1	Dibenzoyl peroxide	105.9[a] / 105[b]	103	2.9	110	– / –5	104.5	1.4	–371.5[a] / –1170.0[b]	–1061.4	–108.6	–1579.0	409.0	–362.5	–8.5
2	Dicumyl peroxide	140.8[a] / 143[b]	141.95	–1.15	144	– / –1	145.3	–4.5	–828.1[a] / –866.0[b]	–896.8	30.8	–798.0	–68.0	–902.5	74.4
3	tert-Butyl peroxy-2-ethylhexanoate	96[b]	100.373	–4.37	105	–9	–	–	–1185.0[b]	–1057.9	–127.1	–1164.0	–21.0	–	–
4	tert-Butyl peroxy-2-ethylhexylcarbonate	125.2[a] / 125[b]	117.02	8.18	116	– / 9	106.3	18.9	–958.4[a] / –1096.0[b]	–1016.7	–79.3	–1208.0	112.0	–1123.2	164.8
5	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane	148[b]	146.13	1.87	123	25	132.8	3.9	–1020.9[a] / –1096.0[b]	–1149.4	–184.6	–1669.0	573.0	–910.3	110.9
6	tert-Butyl peroxypivalate	85[b]	91.13	–6.13	95	–10	–	–	–1150.0[b]	–1181.3	31.3	–1482.0	332.0	–	–
7	Di-(2-ethylhexyl) peroxydicarbonate	65[b]	62.35	2.65	67	–2	–	–	–1003.0[b]	–1131.1	128.1	–1084.0	81.0	–	–
8	Di-tert-Butyl peroxide	139.7[a] / 153[b]	141.95	–2.25	145	– / 8	141.6	–1.9	–1082.5[a] / –1175.0[b]	–1222.4	47.4	–1289.0	114.0	–1023.1	–58.9
9	Dilauroyl peroxide	87[a] / 86[b]	81.433	5.57	73	– / 13	92.2	–5.2	–766.1[a] / –795.0[b]	–564.3	–230.6	–743.0	–52.0	–885.5	119.4
10	tert-Butyl peroxybenzoate	122.7[a] / 121[b]	121.94	0.76	103	– / 18	124.0	–1.3	–1231.0[a] / –1528.0[b]	–1184.8	–343.2	–1532.0	4.0	–980.8	–250.2
11	tert-Butyl cumyl peroxide	150.3[a] / 147[b]	155.97	–5.67	151	– / –4	145.7	4.6	–852.6[a] / –1027.0[b]	–1102.5	75.5	–1036.0	9.0	–970.2	117.6
12	2,5-Dimethyl-2,5-dihydroperoxyhexane	127[b]	124.563	2.44	111	16	–	–	–2622.0[b]	–2684.5	62.5	–	–	–	–
13	1,1-Di-(tert-butyl peroxy)cyclohexane	121.2[a] / 121[b]	124.563	–3.36	118	– / 3	120.4	0.8	–1640.7[a] / –989.0[b]	–1147.1	158.1	–1828.0	839.0	–1367.7	–273.0
14	tert-Amyl peroxy-2-ethylhexyl carbonate	123[b]	117.02	5.98	116	7	–	–	–975.0[b]	–975.6	0.6	–1159.0	184.0	–	–
15	Ethyl-3,3-di-(tert-amyl peroxy) butyrate	140[b]	137.99	2.01	131	9	–	–	–1027.0[b]	–893.3	–133.7	–1696.0	669.0	–	–
16	tert-Amyl peroxy-3,5,5-trimethylhexanoate	118[b]	121.94	–3.94	115	3	–	–	–981.0[b]	–975.6	–5.4	–1141.0	160.0	–	–
17	tert-Butyl peroxyisopropylcarbonate	127[b]	117.02	9.98	114	13	–	–	–1124.0[b]	–1222.4	98.4	–1500.0	376.0	–	–
18	Didecanoyl peroxide	88[b]	81.433	6.57	74	14	–	–	–871.0[b]	–728.8	–142.2	–964.0	93.0	–	–

Table 1 continued

| No.	Name	T_d (exp)/°C	T_d (cal)/°C	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.	ΔH (exp)/ J g^{-1}	ΔH (cal)/ J g^{-1}	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.
19	2,2-Di-(tert-butyl peroxy) butane	137[b]	146.13	−9.13	144	−7	120.6	16.4	−1316.1[a] −1060.0[b]	−1313.9	253.9	−2103.0	1043.0	−1371.5	55.5
20	2,5-Dimethyl-2,5-di-(2-ethylhexanoyl peroxy) hexane	95[b]	85.613	9.39	106	−11	–	–	−1092.0[b]	−948.3	−143.6	−1095.0	3.0	–	–
21	1,1-Di-(tert-amyl peroxy) cyclohexane	121[b]	124.563	−3.56	123	−2	–	–	−1029.0[b]	−1064.9	35.9	−1767.0	738.0	–	–
22	tert-Butyl peracetate	129[b]	121.94	7.06	111	18	116	13	−1519.4[a] −1066.0[b]	−1304.7	238.7	−1672.0	606.0	−1365.8	−153.6
23	2,5-Di(tert-butylperoxy)-2,5-dimethyl-3-hexyne	144[b]	146.13	−2.13	145	−1	–	–	−837.0[b]	−1149.4	312.4	−1692.0	855.0	–	–
24	Dicetyl peroxydicarbonate	63[b]	62.35	0.65	62	1	–	–	−441.0[b]	−473.0	32.0	−382.0	−59.0	–	–
25	Dimyristyl peroxydicarbonate	60[b]	62.35	−2.35	60	0	–	–	−557.0[b]	−637.5	80.5	−606.0	49.0	–	–
26	1,1,3,3-Tetramethylbutyl peroxy-2-ethylhexanoate	92[b]	100.373	−8.37	107	−15	–	–	−834.0[b]	−893.3	59.3	−950.0	116.0	–	–
27	tert-Butyl peroxydiethylacetate	93[b]	100.373	−7.37	106	−13	–	–	−1225.0[b]	−1140.1	−84.9	−1305.0	80.0	–	–
28	1,1,3,3-Tetramethylbutyl hydroperoxide	127[b]	134.403	−7.40	128	−1	–	–	−1545.0[b]	−1670.5	125.5	−1830.0	285.0	–	–
29	3,3,5,7,7-Pentamethyl-1,2,4-trioxepane	180[b]	181.86	−1.86	–	–	–	–	−1523.0[b]	−1695.9	172.9	−1547.0	24.0	–	–
30	Cumene hydroperoxide	169.9[a]	155.97	13.93	–	–	168.2	1.7	−1663.7[a]	−1587.1	−76.6	–	–	−1285.9	−377.8
31	2-Butanone peroxide	87.2[a]	79.136	8.06	–	–	90.6	−3.4	−2299.0[a]	−2236.4	−62.5	–	–	−2548.2	249.2
32	Di-(4-tert-butylcyclohexyl) peroxydicarbonate	85[b]	93.16	−8.16	67	18	–	–	−586.0[b]	−818.1	232.1	−826.6	240.0	–	–
33	Di-(3,5,5-trimethylhexanoyl) peroxide	87[b]	81.433	5.567	75	12	–	–	−767.0[b]	−811.1	44.1	−976.0	209.0	–	–
	The rms deviation			6.06							146.41				
	The σ deviation			5.18							118.19				

[a] Ref [35], [b] Ref [37]

used for constructing and testing of the new model. Table 1 also contains 33 experimental data of different organic peroxides with simple molecular structures, which were used as training set. The study of organic peroxides has indicated that it is possible to express the heat of decomposition of these compounds as a function of several structural parameters. Multiple linear regression method was used to obtain the relationship between heat of decomposition and molecular structure in Eq. (2) [69] as:
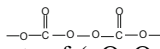
$$\Delta H_{\text{Dec}} = -1551.45 + 41.13 n_{\text{C}} - 1014.05 \delta_{(\text{HO}-\text{O}\cdots-\text{O}-\text{OH})} \\ - 640.13\alpha - 857.68\beta$$

(2)

where ΔH_{Dec} is the heat of decomposition in J g^{-1}; n_{C} represents the number of carbon in molecular formula; and $\delta_{(\text{HO}-\text{O}-\cdots-\text{O}-\text{OH})}$ is 1.0 for the presence of two hydroperoxy functional groups in the molecular structure. The presence of some molecular fragments may also affect the values of ΔH_{Dec} which are incorporated in α and β as nonadditive structural parameters.

Definition of α

For the presence of aromatic cycles, non-aromatic cycles and non-aromatic cycles with methyl substitution in them, the values of α are 0.1, 0.2 and 0.6, respectively. If organic peroxide has the ⟨fragment⟩ fragment in its structure, the value of α is 2.

Definition of β

For the presence of molecular fragment ⟨fragment⟩ in acyclic peroxides, β is 0.5. If two fragments of (–O–O–R) or ⟨fragment⟩ exist, the value of β will be 0.4 or 0.6, respectively.

Results and discussion

Roles of different variables

As seen in Eq. (1), the coefficients of n_{O}, $\lambda_{\text{C}=\text{O}}$ and λ_{sym} have negative signs, which confirm that higher values of these parameters can reduce the values of T_{Dec}. For the presence of several molecular fragments given in λ', this reduction may be enhanced. However, the predicted results of Eq. (1) have confirmed that the number of oxygen atoms in the formula of organic peroxides has an important contribution in prediction of their decomposition temperature as well as their melting point [70]. The variable n_{O} in Eq. (1) is also an important factor to evaluate hazards reactivity of energetic compounds [21–23]. The presence of λ_{sym} term in Eq. (1) confirms that the decomposition process of peroxides is strongly affected by reactivity of the formed radicals [26, 28]. It was shown that the presence of some polar functional groups such as –O–C(O)–OO–(CO)–O– or –C(O)–OO–(CO)– given in λ' can influence the thermal stability of organic peroxides like their melting points [70]. Positive sign of the number of carbon atoms in Eq. (2) shows that heat of decomposition of organic peroxides can increase with increasing the number of carbon atom. Meanwhile, the existence of two hydroperoxy functional groups in the molecular structure of organic peroxides can reduce their heat of decomposition.

Table 2 Standardized coefficients and some statistical parameters of Eq. (1)

Variable	Coefficient	Standard error	Lower bound (95 %)	Upper bound (95 %)
Intercept	165.8090	3.0826	159.5571	172.0609
n_{O}	−4.9175	0.9099	−6.7629	−3.0721
$\lambda_{\text{C}=\text{O}}$	−29.1104	2.3123	−33.8000	−24.4209
λ_{sym}	−14.0170	2.3539	−18.7908	−9.2432
λ'	−30.8133	1.8957	−34.6580	−26.9686

Table 3 Standardized coefficients and some statistical parameters of Eq. (2)

Variable	Coefficient	Standard error	Lower bound (95 %)	Upper bound (95 %)
Intercept	−1551.4	63.3	−1679.8	−1423.0
n_{C}	41.1	4.0	32.9	49.3
$\delta_{(\text{HO}-\text{O}-\cdots-\text{O}-\text{OH})}$	−1014.0	118.6	−1254.5	−773.5
α	−640.1	101.8	−846.5	−433.7
β	−857.7	75.7	−1011.2	−704.1

Table 4 Comparison of the predicted decomposition onset temperature of several organic peroxides containing complex molecular structures by Eq. (1), Lu et al. [38] and Prana et al. [40] with experimental data as test set

Name	T_d(exp)/ °C	T_d(cal)/ °C	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.	ΔH (exp)/ J g^{-1}	ΔH (cal)/ J g^{-1}	Dev.	Prana et al. method	Dev.	Lu et al. method	Dev.
tert-Butyl peroxy-3,5,5-trimethylhexanoate	114[b]	121.94	−7.94	112	2	–	–	−869.0[b]	−1016.7	147.7	−1186.0	317.0	–	–
tert-Amyl peroxy-2-ethylhexanoate	98[b]	100.37	−2.373	109	−11	–	–	−1067.0[b]	1016.7	−50.3	−1111.0	44.0	–	–
Di-tert-Amyl peroxide	149[b]	141.95	7.05	145	4	–	–	−1086.0[b]	−1140.1	54.13	−1181.0	95.0	–	–
tert-Amyl hydroperoxide	143[b]	134.40	8.597	127	16	–	–	−1993.0[b]	−1793.9	−199.1	−2081.0	88.0	–	–
tert-Butyl hydroperoxide	156.3[a]	155.97	0.33	128	–	159.1	−2.8	−717.9[a]	−1386.9	0.9	−2124.0	738.0	−1646.7	928.8
	91[b]				−37			−1386.0[b]						
1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane	118.7[a]	124.56	−5.863	118	–	119.4	−0.7	−1411.5[a]	−1366.8	−137.2	−1597.0	93.0	−1362.9	−48.6
	120[b]				2			−1504.0[b]						
Di-n-propyl peroxydicarbonate	53[b]	62.35	−9.35	61	−8	–	–	−1824.0[b]	−1542.5	−281.5	−1844.0	20.0	–	–
2,4-Pentanedione peroxide	117.3[a]	123.97	−6.67	–	–	117.4	−0.1	−2887.7[a]	−2855.5	−32.2	–	–	−2771.7	−116.0
The rms deviation		6.70							144.1					
The σ deviation		6.02							113.0					

[a] Ref [35], [b] Ref [37]

Table 5 Several statistical parameters of the new models

Property	rms	σ	Q^2 – CV	R^2
Equation (1)	6.06/°C	5.18/°C	0.955	0.956
Equation (2)	146.41/J g^{-1}	118.19/J g^{-1}	0.912	0.916

Reliability of the predicted results and model validation

The R^2 values or the coefficients of determination of Eqs. (1) and (2) are 0.959 and 0.916, respectively. As seen in Table 1, the predicted decomposition temperatures of organic peroxides have a root-mean-square (rms) and the average absolute deviations (σ) of 6.06 and 5.18 °C, respectively. Moreover, deviation of the estimated onset temperature is more than 10 °C only for one compound. The values of rms and σ of Eq. (2) for the heat of decomposition are 146.41 and 118.19 J g^{-1}, respectively. Tables 2 and 3 indicate statistical parameters of Eqs. (1) and (2), which allow comparing the relative weight of the

variables in both models. Standard error shows a measure of the precision of the estimation of a coefficient that can determine precision over repeated measurements. The p value can assess the significance of an observed effect or variation. For p value <0.05, it may confirm that the observed effect is not due to random variations and the effect is significant. In this work, the p values for two models are near to zero. Thus, suitable statistical parameters and relatively good R^2 value validate that the predicted results of these new methods are in good agreement with experimental values.

Table 4 contains further eight organic peroxides with complex molecular structures, which have been used for external validation of these new models. As seen in Table 4, the new proposed methods give relatively good results that confirm high reliability of the new models. The comparison of predicted results of Eqs. (1) and (2) is shown in Tables 1 and 4 with Lu et al. [38] and Prana et al. [40] models as two of the best available QSPR methods, which are based on complex molecular descriptors. Table 5 summarizes several important statistical parameters of two

Table 6 Comparison of the several statistical and validation parameters of the proposed correlations with Lu et al. [14] and Prana et al. [16] models

General properties	Equation (1)	Prana et al. method	Lu et al. method	Equation (2)	Prana et al. method	Lu et al. method
Number of applied independent variables	3	3	4	2	4	4
Number of training test	33	25	16	33	25	16
Number of test set	8	13	–	8	13	–
Kind of descriptors	The number of oxygen atom, the presence of carbonyl group and the existence of same fragments attached to the –O–O– bond	The number of peroxide bonds, average local Fukui function on O atoms of the peroxide bond and the eV energy difference between the LUMO and HOMO orbitals	Dissociation energy, bond length of the oxygen–oxygen bond, the number of peroxide function groups and molecular hardness	The number of carbon atom and the presence of di-hydroperoxy fragments in the molecule	The concentration of the target peroxide, the average NBO charges for an oxygen in the –O–O– bond, the local softness on the HOMO orbital of oxygen in the –O–O– bond and the rotational entropy at 300 K	The atomic charge of oxygen, dissociation energy of oxygen–oxygen bond, the number of functional groups and molecular weight
R^2 (training, test and cross-validation)	0.959, 0.973, 0.955	0.84, 0.80, 0.77	0.916, –, 0.108	0.916, 0.912,0.991	0.90, 0.32, 0.83	0.921, –, 0.811
The rms deviation of training set (and test set)	6.06 (6.70 °C)	14 °C (–)	–	146.41 J g^{-1} (144.1 J g^{-1})	113 J g^{-1} (358 J g^{-1})	–

new proposed models. As indicated in Table 5, the internal validation of proposed new model has been checked by applying the cross-validation test in which the leave-more-out (25 % out) cross-validation, denoted as $Q^2 - CV$, was employed.

Table 6 shows the comparison of statistical parameters of training and test sets of Eqs. (1) and (2) with Lu et al. [38] and Prana et al. [40] models, which confirm higher reliability of the new correlation. As indicated in Table 6, the internal validation of proposed new model has been checked by applying the cross-validation test in which the leave-more-out (25 % out) cross-validation was employed. Since the strong models are expected to show a low difference between $Q^2 - CV$ and R^2 coefficients [71, 72], Eqs. (1) and (2) satisfy these conditions.

Figures 1 and 2 shows the correlation of the predicted results of Eq. (1) and (2) with experimental data of organic peroxides, which is reported in Tables 1 and 4. Thus, as shown in Tables 1, 4 and 6, the new relationships give good results for estimation of decomposition onset temperature
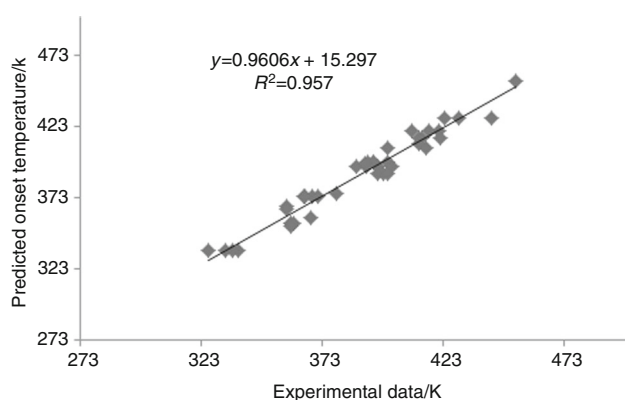

Fig. 1 Predicted decomposition onset temperature of organic peroxides versus experimental data for both training and test sets, which are given in Tables 1 and 4
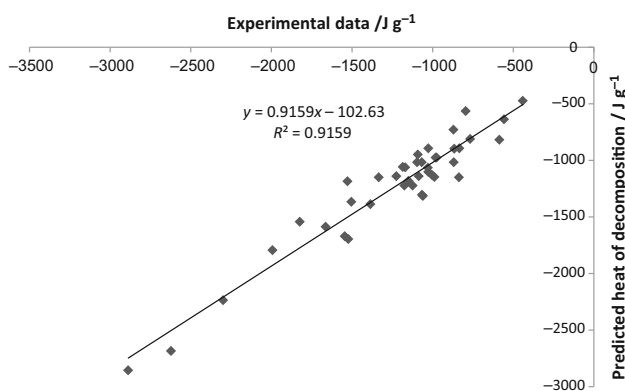

Fig. 2 Predicted heat of decomposition of organic peroxides versus experimental data for both training and test sets, which are introduced in Tables 1 and 4

and heat of decomposition of organic peroxides with respect to the models of Lu et al. [38] and Prana et al. [40], which are based on complex quantum mechanical descriptors.

Conclusions

In this study, two new reliable relationships were introduced for prediction of onset decomposition temperature and heat of decomposition of organic peroxides on the basis of their molecular structures. These novel correlations can predict decomposition onset temperature of organic peroxides and heat of decomposition of organic peroxides using three and two descriptors, respectively. In contrast to the other available QSPR models, which are based on complex molecular descriptors, the descriptors of Eqs. (1) and (2) can be easily found on the basis of the molecular structure of desired organic peroxide. Thus, the new proposed methods can be applied for the prediction of thermal stability parameters of any new organic peroxides only from their molecular structures. It was shown that the number of carbon and oxygen atoms as well as the presence of carbonyl or two hydroperoxy functional groups has significant effect on the thermal stability of organic peroxides. The suitable statistical parameters and relatively good R^2 values of Eqs. (1) and (2) showed that these new methods are reliable. Moreover, they have a good predictive power for the estimation of thermal stability of organic peroxides as compared to the best available methods.

References

1. Klapötke TM. Chemistry of high-energy materials. 3rd ed. Berlin: De Gruyter; 2015.
2. Agrawal JP. High energy materials: propellants, explosives and pyrotechnics. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA; 2010.
3. Pilar R, Pachman J, Matyáš R, Honcová P, Honc D. Comparison of heat capacity of solid explosives by DSC and group contribution methods. J Therm Anal Calorim. 2015;121(2):683–9.
4. Pourmortazavi SM, Sadri M, Rahimi-Nasrabadi M, Shamsipur M, Jabbarzade Y, Khalaki MS, et al. Thermal decomposition kinetics of electrospun azidodeoxy cellulose nitrate and polyurethane nanofibers. J Therm Anal Calorim. 2015;119(1):281–90.
5. Pouretedal H, Ravanbod M. Kinetic study of ignition of Mg/NaNO3 pyrotechnic using non-isothermal TG/DSC technique. J Therm Anal Calorim. 2015;119(3):2281–8.
6. Yan QL, Zeman S. Theoretical evaluation of sensitivity and thermal stability for high explosives based on quantum chemistry methods: a brief review. Int J Quantum Chem. 2013;113 (8):1049–61.

7. Badgujar D, Talawar M, Asthana S, Mahulikar P. Advances in science and technology of modern energetic materials: an overview. J Hazard Mater. 2008;151(2):289–305.

8. Talawar M, Sivabalan R, Mukundan T, Muthurajan H, Sikder A, Gandhe B, et al. Environmentally compatible next generation green energetic materials (GEMs). J Hazard Mater. 2009;161 (2):589–607.

9. Keshavarz MH, Moradi S, Saatluo BE, Rahimi H, Madram AR. A simple accurate model for prediction of deflagration temperature of energetic compounds. J Therm Anal Calorim. 2013;112 (3):1453–63.

10. Keshavarz MH, Ghani K, Asgari A. A new method for predicting heats of decomposition of nitroaromatics. Zeitschrift für anorganische und allgemeine Chemie. 2015;641(10):1818–23.

11. Keshavarz MH, Ghani K, Asgari A. A suitable computer code for prediction of sublimation energy and deflagration temperature of energetic materials. J Therm Anal Calorim. 2015;121(2):675–81.

12. Keshavarz MH, Motamedoshariati H, Moghayadnia R, Ghanbarzadeh M, Azarniamehraban J. A new computer code for assessment of energetic materials with crystal density, condensed phase enthalpy of formation, and activation energy of thermolysis. Propellants Explos Pyrotech. 2013;38(1):95–102.

13. Chen ZX, Xiao HM. Quantum chemistry derived criteria for impact sensitivity. Propellants Explos Pyrotech. 2014;39(4):487–95.

14. Fang-qiang Y, Cong-zhong C, Shuai Z. Prediction of impact sensitivity of nitro energetic compounds by using structural parameters. Explos Shock Waves. 2013;1:012.

15. Fayet G, Rotureau P. Development of simple QSPR models for the impact sensitivity of nitramines. J Loss Prev Process Ind. 2014;30:1–8.

16. Keshavarz MH. A new general correlation for predicting impact sensitivity of energetic compounds. Propellants Explos Pyrotech. 2013;38(6):754–60.

17. Keshavarz MH, Motamedoshariati H, Pouretedal HR, Tehrani MK, Semnani A. Prediction of shock sensitivity of explosives based on small-scale gap test. J Hazard Mater. 2007;145(1):109–12.

18. Keshavarz MH, Hayati M, Ghariban-Lavasani S, Zohari N. A new method for predicting the friction sensitivity of nitramines. Central Eur J Energ Mater. 2015;12(2):215–27.

19. Wang R, Sun L, Kang Q, Li Z. Predicting the electric spark sensitivity of nitramines from molecular structures via support vector machine. J Loss Prev Process Ind. 2013;26(6):1193–7.

20. Keshavarz MH. Theoretical prediction of electric spark sensitivity of nitroaromatic energetic compounds based on molecular structure. J Hazard Mater. 2008;153(1):201–6.

21. Zohari N, Keshavarz MH, Seyedsadjadi SA. A link between impact sensitivity of energetic compounds and their activation energies of thermal decomposition. J Therm Anal Calorim. 2014;117(1):423–32.

22. Zohari N, Keshavarz MH, Seyedsadjadi SA. A novel method for risk assessment of electrostatic sensitivity of nitroaromatics through their activation energies of thermal decomposition. J Therm Anal Calorim. 2014;115(1):93–100.

23. Keshavarz MH, Zohari N, Seyedsadjadi SA. Relationship between electric spark sensitivity and activation energy of the thermal decomposition of nitramines for safety measures in industrial processes. J Loss Prev Process Ind. 2013;26(6):1452–6.

24. Keshavarz MH, Hayati M, Ghariban-Lavasani S, Zohari N. Relationship between activation energy of thermolysis and friction sensitivity of cyclic and acyclic nitramines. Zeitschrift für anorganische und allgemeine Chemie. 2016;642(2):182–8.

25. Matyáš R, Pachman J. Organic peroxides. In: Primary explosives. Berlin: Springer; 2013. p. 255–87.

26. Benassi R, Folli U, Sbardellati S, Taddei F. Conformational properties and homolytic bond cleavage of organic peroxides. I. An empirical approach based upon molecular mechanics and ab initio calculations. J Comput Chem. 1993;14(4):379–91.

27. Smith MB, March J. March's advanced organic chemistry: reactions, mechanisms, and structure. Berlin: Wiley; 2007.

28. Benassi R, Taddei F. Homolytic bond-dissociation in peroxides, peroxyacids, peroxyesters and related radicals: ab initio MO calculations. Tetrahedron. 1994;50(16):4795–810.

29. Chang R, Tseng J, Jehng J, Shu C, Hou H. Thermokinetic model simulations for methyl ethyl ketone peroxide contaminated with H₂SO₄ or NaOH by DSC and VSP2. J Therm Anal Calorim. 2006;83(1):57–62.

30. Tsai L-C, You M-L, Ding M-F, Shu C-M. Thermal hazard evaluation of lauroyl peroxide mixed with nitric acid. Molecules. 2012;17(7):8056–67.

31. CSB, HI. Improving reactive hazard management. Washington, DC: US Chemical Safety and Hazard Investigation Board; 2002.

32. Ho TC, Duh YS, Chen J. Case studies of incidents in runaway reactions and emergency relief. Process Saf Prog. 1998;17 (4):259–62.

33. Kletz TA. Fires and explosions of hydrocarbon oxidation plants. Plant/Oper Prog. 1988;7(4):226–30.

34. Martin JJ. SAFETY—tert-Butyl peracetate—an explosive compound. Ind Eng Chem. 1960;52(4):65A–8A.

35. Wakakura M, Iiduka Y. Trends in chemical hazards in Japan. J Loss Prev Process Ind. 1999;12(1):79–84.

36. Noller D, Mazurowski S, Linden G, De Leeuw F, Mageli O. A relative hazard classification of organic peroxides. Ind Eng Chem. 1964;56(12):18–27.

37. Gao Y, Xue Y, Lǚ Z-g, Wang Z, Chen Q, Shi N, et al. Self-accelerating decomposition temperature and quantitative structure–property relationship of organic peroxides. Process Saf Environ Prot. 2015;94:322–8.

38. Lu Y, Ng D, Mannan MS. Prediction of the reactivity hazards for organic peroxides using the QSPR approach. Ind Eng Chem Res. 2010;50(3):1515–22.

39. Pan Y, Zhang Y, Jiang J, Ding L. Prediction of the self-accelerating decomposition temperature of organic peroxides using the quantitative structure–property relationship (QSPR) approach. J Loss Prev Process Ind. 2014;31:41–9.

40. Prana V, Rotureau P, Fayet G, André D, Hub S, Vicot P, et al. Prediction of the thermal decomposition of organic peroxides by validated QSPR models. J Hazard Mater. 2014;276:216–24.

41. Her B, Jones A, Wollack JW. A three-step synthesis of benzoyl peroxide. J Chem Educ. 2014;91(9):1491–4.

42. Li X-R, Koseki H. Thermal decomposition kinetic of liquid organic peroxides. J Loss Prev Process Ind. 2005;18(4):460–4.

43. Malow M, Wehrstedt K. Prediction of the self-accelerating decomposition temperature (SADT) for liquid organic peroxides from differential scanning calorimetry (DSC) measurements. J Hazard Mater. 2005;120(1):21–4.

44. Saraf S, Rogers W, Mannan MS. Prediction of reactive hazards based on molecular structure. J Hazard Mater. 2003;98(1):15–29.

45. Pourmortazavi SM, Rahimi-Nasrabadi M, Kohsari I, Hajimirsadeghi SS. Non-isothermal kinetic studies on thermal decomposition of energetic materials: KNF and NTO. J Therm Anal Calorim. 2011;110(2):857–63.

46. Keshavarz MH, Zohari N, Seyedsadjadi SA. Validation of improved simple method for prediction of activation energy of the thermal decomposition of energetic compounds. J Therm Anal Calorim. 2013;114(2):497–510.

47. Pandele Cusu J, Musuc AM, Matache M, Oancea D. Kinetics of exothermal decomposition of some. J Therm Anal Calorim. 2011;110(3):1259–66.

48. Krabbendam-LaHaye E, De Klerk W, Krämer R. The kinetic behaviour and thermal stability of commercially available explosives. J Therm Anal Calorim. 2005;80(2):495–501.

49. Bunyan P, Baker C, Turner N. Application of heat conduction calorimetry to high explosives. Thermochim Acta. 2003;401 (1):9–16.

50. Keshavarz MH. Simple method for prediction of activation energies of the thermal decomposition of nitramines. J Hazard Mater. 2009;162(2):1557–62.

51. Keshavarz MH, Pouretedal HR, Shokrolahi A, Zali A, Semnani A. Predicting activation energy of thermolysis of polynitro arenes through molecular structure. J Hazard Mater. 2008;160(1):142–7.

52. Keshavarz M. A new method to predict activation energies of nitroparaffins. Indian J Eng Mater Sci. 2009;16(6):429.

53. Gharagheizi F, Sattari M, Ilani-Kashkouli P, Mohammadi AH, Ramjugernath D, Richon D. Quantitative structure—property relationship for thermal decomposition temperature of ionic liquids. Chem Eng Sci. 2012;84:557–63.

54. Zhang Q. Shreeve JnM. Energetic ionic liquids as explosives and propellant fuels: a new journey of ionic liquid chemistry. Chem Rev. 2014;114(20):10527–74.

55. Wang Q, Wang J, Larranaga MD. Simple relationship for predicting onset temperatures of nitro compounds in thermal explosions. J Therm Anal Calorim. 2013;111(2):1033–7.

56. Keshavarz M, Pouretedal H, Semnani A. Relationship between thermal stability and molecular structure of polynitro arenes. Indian J Eng Mater Sci. 2009;16(1):61.

57. Yang T, Chen L, Chen W, Zhou Y, Gao H, Zhong T. Thermal stability of 2-ethylhexyl nitrate with acid. J Therm Anal Calorim. 2015;119(1):205–12.

58. Xing X, Zhao S, Huang W, Li W, Zhang W, Diao X, et al. Thermal decomposition behavior of hexanitrohexaazaisowurtzitane and its blending with BTATz (expand) and Al by microcalorimetry. J Therm Anal Calorim. 2015;120(2):1393–7.

59. Pilar R, Pachman J, Matyáš R, Honcová P, Honc D. Comparison of heat capacity of solid explosives by DSC and group contribution methods. J Therm Anal Calorim. 2015;121(2):683–9.

60. Xiao L-B, Zhao F-Q, Luo Y, Gao H-X, Li N, Meng Z-H et al. Thermal behavior and safety of 4, 10-dinitro-2, 6, 8, 12-tetraoxa-4, 10-diazaisowutrzitane. J Therm Anal Calorim. 2015;121(2):839–42.

61. Huang H, Shi Y, Yang J. Thermal characterization of the promising energetic material TKX-50. J Therm Anal Calorim. 2015;121(2):705–9.

62. Künzel M, Yan Q-L, Šelešovský J, Zeman S, Matyáš R. Thermal behavior and decomposition kinetics of ETN and its mixtures with PETN and RDX. J Therm Anal Calorim. 2014;115(1):289–99.

63. Fischer D, Klapötke TM, Stierstorfer J. Oxalylhydrazinium nitrate and dinitrate—efficiency meets performance. J Energ Mater. 2014;32(1):37–49.

64. Klapötke TM. Chemistry of high-energy materials. Berlin: Walter de Gruyter; 2012.

65. Agrawal JP, Hodgson R. Organic chemistry of explosives. Chichester: Wiley; 2007.

66. Felix SP, Singh G, Sikder A, Aggrawal J. Studies on energetic compounds: Part 33: thermolysis of keto-RDX and its plastic bonded explosives containing thermally stable polymers. Thermochim Acta. 2005;426(1):53–60.

67. Sikder A, Sikder N. A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications. J Hazard Mater. 2004;112(1):1–15.

68. Talawar M, Jangid S, Nath T, Sinha R, Asthana S. New directions in the science and technology of advanced sheet explosive formulations and the key energetic materials used in the processing of sheet explosives: Emerging trends. J Hazard Mater. 2015;300:307–21.

69. Palm WJ. Introduction to MATLAB 7 for engineers. New York: McGraw-Hill; 2005.

70. Khozani MH, Keshavarz MH, Nazari B, Mohebbi M. Simple approach for prediction of melting points of organic molecules containing hazardous peroxide bonds. J Iran Chem Soc. 2015;12 (4):587–98.

71. Gramatica P. Principles of QSAR models validation: internal and external. QSAR Comb Sci. 2007;26(5):694.

72. Tropsha A. Best practices for QSAR model development, validation, and exploitation. Mol Inf. 2010;29(6–7):476–88.