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ORIGINAL PAPER

Simple approach for prediction of melting points of organic molecules containing hazardous peroxide bonds

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Abstract In this work, a new and simple method is proposed to estimate the melting points of hazardous organic peroxide compounds including hydroperoxides, dialkyl peroxides, primary and secondary ozonides, peroxyacids, diacyl peroxides and alkyl peroxyesters compounds. This method can be applied for any peroxide compound with general formula $C_xH_yO_z$ to predict its melting point on the basis of elemental composition and specific structural moieties as additive and non-additive functions. It was applied for 104 different peroxide compounds including complex molecular structures. The predicted results give more reliable results in comparison to two of the best available methods. The average and maximum percent deviations of the new method are 6.8 and 21.1, respectively, which are lower than corresponding predicted values of Joback–Reid (24.1 and 101.9) and Jain–Yalkowsky (25.4 and 211.1).

Keywords Melting point · Peroxide compound · Correlation · Safety

List of symbols

$T_{m,peroxide}$	Melting points of peroxide compound
T_{core}	Additive core function
$T_{correcting}$	Non-additive molecular fragments
$T^{+}_{m,peoroxide}$	Positive contribution of structural parameters in $T_{correcting}$
$T^{-}_{m,peoroxide}$	Negative contribution of structural parameters in $T_{correcting}$
n_C	The number of carbon atoms
n_H	The number of hydrogen atoms
n_O	The number of oxygen atoms

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Introduction

The debate about new energetic compounds with suitable thermodynamic properties, performance and sensitivity is of utmost importance to scientists. Moreover, synthesis and measuring of properties of energetic compounds are dangerous, expensive, time consuming or sometimes impossible [1].

Prediction of melting point of energetic materials can be done by quantum mechanical calculations [2–5]. This approach has been considered difficult through simulation because of the presence of the free energy barrier for the formation of a liquid–solid interface. Methods based on quantitative structure property (QSPR) and some empirical models have been developed for organic molecules including a number of drugs and/or homologous series [6–13].

For energetic materials, computer codes and empirical methods can help to improve systematic and scientific formulation of appropriate futuristic target molecules having enhanced performance as well as good thermal stability, impact and friction sensitivity. Empirical methods can be used to confirm the computer output through desk calculations of performance and physicochemical properties of energetic compounds. Due to the expenditure connected with the development and synthesis of a new energetic material [14–16], development of reliable methods is essential for prediction of desired properties of energetic materials, e.g., enthalpy of fusion [17–22].

Moreover, the knowledge of physical properties and performance of energetic materials can be useful for new and complex synthesis.

Prediction of melting point is important for using in chemical identification, purification and calculation of the other physicochemical properties such as vapor pressure and aqueous solubility [12]. Group contribution methods can be used to estimate melting points of different classes of organic compounds [23], which are based on the sum of contributions of small groups of atoms constituting the molecule. For example, some group contribution methods are Lydersen [24], Ambrose [25], Klincewicz and Reid [26], Joback and Reid [27], Lyman et al. [28], Horvath [29], Prickett et al. [30], Constantinou et al. [31–33], Marrero-Morej´on and Pardillo-Fontdevilla [34], Marrero and Gani [35]. However, in contrast to the other physicochemical properties, prediction of melting points was not very well estimated by the group contribution methods [6, 24, 36, 37]. In addition, there is no reliable method for predicting melting points of hazardous materials containing peroxide bonds.

The purpose of this work is to introduce a new simple model for prediction of melting points of organic peroxides, which can be classified according to their molecular structures as hydroperoxides, dialkyl peroxides, α-oxygen substituted alkyl hydroperoxides and dialkyl peroxides, primary and secondary ozonides, peroxyacids, diacyl peroxides (acyl and organosulfonyl peroxides), and alkyl peroxyesters (peroxycarboxylates, peroxysulfonates and peroxyphosphates) [38]. The predicted results of the new model were also compared with two of the best available methods, e.g., Joback–Reid (JR) [27] and Jain–Yalkowsky (JY) [10] methods.

Results and discussion

The study of various organic compounds containing peroxide bonds has shown that the elemental composition has an important contribution in prediction of their melting point. The study of compounds containing –O–O– groups has indicated that it is possible to express the melting points of these compounds as core and correcting functions [37]:

$$T_{\mathrm{m,peroxide}} = T_{\mathrm{core}} + T_{\mathrm{correcting}} \quad (1)$$

where $T_{\mathrm{m,peroxide}}$, T_{core} and $T_{\mathrm{correcting}}$ are melting points of peroxide compound, core and correcting functions, respectively. The parameter T_{core} is due to the contribution of elemental composition. The factor $T_{\mathrm{correcting}}$ is a correcting function that can be specified on the basis of molecular structure of desired peroxide molecule. The presence of some specific polar groups such as –OH or more than one peroxy acid groups without any functional groups may enhance intermolecular interactions. In contrast, the presence of some specific molecular moieties under certain conditions can decrease molecular attractions. Table 1 contains experimental data of melting points for 104 peroxide organic compounds, which have been used to optimize Eq. (1) with respect to different functional groups and molecular fragments. Multiple linear regression method was used to obtain the relative contributions of elemental composition in T_{core} and molecular moieties in $T_{\mathrm{non\,-\,add}}$ [37]. However, a general correlation for any peroxide organic compound can be introduced as:

$$T_{\mathrm{m,peroxide}} = 280.5 + 5.159\,T_{\mathrm{core}} + 38.90\,T_{\mathrm{correcting}} \quad (2)$$

$$T_{\mathrm{core}} = n_{\mathrm{C}} - 0.556 n_{\mathrm{H}} + 2.064 n_{\mathrm{O}} \quad (3)$$

$$T_{\mathrm{correcting}} = T^{+}_{\mathrm{m,peoroxide}} - 1.345\,T^{-}_{\mathrm{m,peoroxide}} \quad (4)$$

where n_{C}, n_{H} and n_{O} are the number of carbon, hydrogen and oxygen atoms, respectively; $T^{+}_{\mathrm{m,peoroxide}}$ and $T^{-}_{\mathrm{m,peoroxide}}$ are the positive and negative contributions of structural parameters in $T_{\mathrm{correcting}}$, respectively. As seen in Eq. (2), two parameters $T^{+}_{\mathrm{m,peoroxide}}$ and $T^{-}_{\mathrm{m,peoroxide}}$ can correct the values obtained on the basis of the contribution of elemental composition for the existence of several molecular fragments.

Two parameters $T^{+}_{\mathrm{m,peoroxide}}$ and $T^{-}_{\mathrm{m,peoroxide}}$

For the presence of several molecular moieties, the values of $T^{+}_{\mathrm{m,peoroxide}}$ and $T^{-}_{\mathrm{m,peoroxide}}$ can be specified.

Prediction of $T^{+}_{\mathrm{m,peoroxide}}$

The existence of hydrogen bonding polar –OH or more than one peroxy acid groups without any functional groups can lead to much more efficient packing and the attractive forces confining the respective species in the crystal lattice. This situation was also confirmed in previous studies for different classes of energetic compounds [39]. For different aromatic and non-aromatic organic compounds containing these molecular moieties, there is a reinforced intermolecular hydrogen bond. Since dipole moment is an important factor for controlling the melting point, the sum of local dipole moments has a more pronounced effect than net dipole moment on melting point for some specific molecular fragments. The values of $T^{+}_{\mathrm{m,peoroxide}}$ are 2.0 and 0.5 for the existence of more than one peroxy acid group without any functional groups and –OH, respectively.

Prediction of $T^{-}_{\mathrm{m,peoroxide}}$

For some organic molecules including –(CO)OO– and –O–C(O)–OO–(CO)–O– groups, the values of T_{core} are

Table 1 Comparison of the predicted melting points (K) of organic peroxides by new, JR [27] and JY [10] methods with experimental data

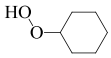
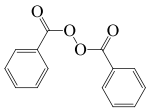
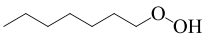
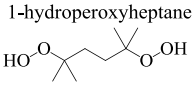
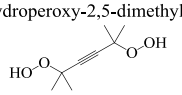
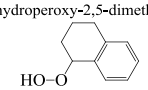
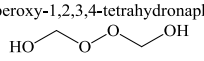
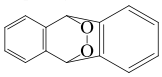
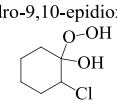
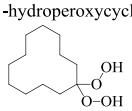
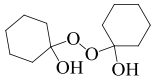
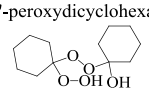
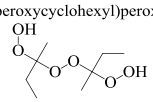
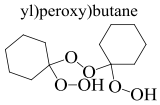
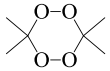
No.	Peroxide compound	Exp[37]	New method	Dev.	JR method	Dev.	JY method	Dev.
1	 2-hydroperoxy-2-methylpropane	277	294	-5.9	220	20.6	231	16.8
2	 hydroperoxycyclohexane	253	298	-17.8	248	2.1	367	-45.0
3	 benzoic peroxyanhydride	380	367	3.4	371	2.4	386	-1.7
4	 1-hydroperoxyheptane	309	292	5.4	290	6.0	278	9.8
5	 2,5-dihydroperoxy-2,5-dimethylhexane	378	391	-3.3	258	31.8	367	2.9
6	 2,5-dihydroperoxy-2,5-dimethylhex-3-yne	381	402	-5.5	364	4.5	432	-13.4
7	 1-hydroperoxy-1,2,3,4-tetrahydronaphthalene	329	319	3.1	294	10.6	371	-12.7
8	 peroxydimethanol	367	336	8.5	234	36.2	378	-3.1
9	 9,10-dihydro-9,10-epidioxyanthracene	393	345	12.2	421	7.2	376	4.4
10	 2-chloro-1-hydroperoxycyclohexanol	349	331	5.1	354	1.4	558	-59.8
11	 1,1-dihydroperoxycyclododecane	413	394	4.7	401	2.9	842	-103.8
12	 1,1'-peroxydicyclohexanol	343	341	0.5	454	32.2	559	-62.9
13	 1-((1-hydroperoxycyclohexyl)peroxy)cyclohexanol	350	352	-0.7	636	81.8	480	-37.3
14	 2-hydroperoxy-2-((2-hydroperoxybutan-2-yl)peroxy)butane	314	334	-6.5	302	3.6	368	-17.3
15	 1,1'-peroxybis(1-hydroperoxycyclohexane)	356	343	3.5	619	74.2	453	-27.4
16	 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane	405	320	21.1	315	22.4	462	-14.0

Table 1 continued

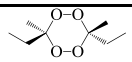
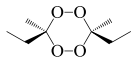
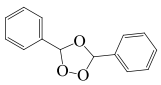
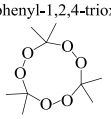
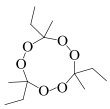
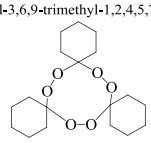
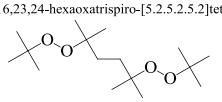
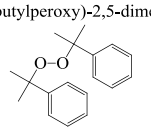
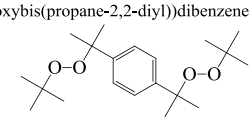
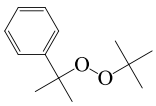
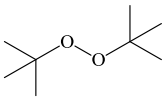
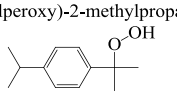
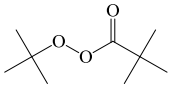
17	 (3*r*,6*r*)-3,6-diethyl-3,6-dimethyl-1,2,4,5-tetraoxane	297	318	-7.3	337	13.6	477	-60.8
18	 (3*s*,6*s*)-3,6-diethyl-3,6-dimethyl-1,2,4,5-tetraoxane	286	318	-11.3	337	17.8	433	-51.3
19	 3,5-diphenyl-1,2,4-trioxolane	346	322	7.1	387	11.7	488	-41.0
20	 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxonane	370	339	8.2	411	11.1	519	-40.4
21	 3,6,9-triethyl-3,6,9-trimethyl-1,2,4,5,7,8-hexaoxonane	304	337	-10.9	444	46.1	665	-118.6
22	 7,8,15,16,23,24-hexaoxatrispiro-[5.2.5.2.5.2]tetracosane	366	351	4.1	739	101.9	1139	-211.1
23	 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane	281	308	-9.6	369	31.1	312	-11.0
24	 (peroxybis(propane-2,2-diyl))dibenzene	314	332	-5.7	395	25.9	377	-20.2
25	 1,4-bis(2-(*tert*-butylperoxy)propan-2-yl)benzene	352	329	6.7	453	28.5	454	-28.9
26	 (2-(*tert*-butylperoxy)propan-2-yl)benzene	286	311	-8.8	266	7.2	211	26.3
27	 2-(*tert*-butylperoxy)-2-methylpropane	255	291	-14.2	229	10.2	362	-41.9
28	 1-(2-hydroperoxypropan-2-yl)-4-isopropylbenzene	307	312	-1.8	316	2.9	340	-10.9
29	 *tert*-butyl 2,2-dimethylpropaneperoxoate	255	255	0.1	290	13.8	300	-17.6

Table 1 continued

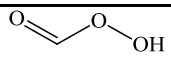
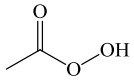
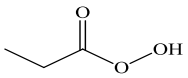
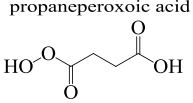
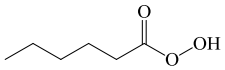
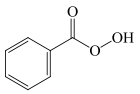
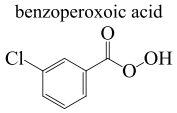
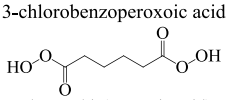
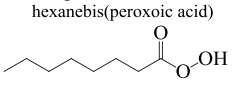
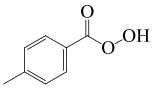
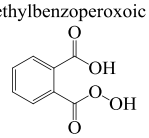
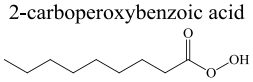
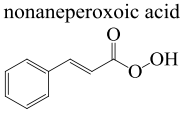
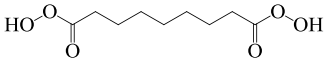
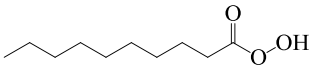
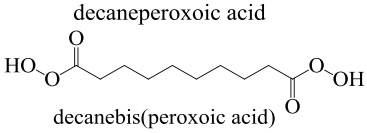
30	 methaneperoxoic acid	255	260	-1.7	221	13.6	225	11.8
31	 Peroxyacetic acid	273	259	5.2	215	21.1	287	-5.1
32	 propaneperoxoic acid	260	258	0.7	215	17.2	262	-0.7
33	 4-hydroperoxy-4-oxobutanoic acid	380	337	11.3	399	4.8	363	4.5
34	 hexaneperoxoic acid	288	309	-7.2	261	9.6	298	-3.4
35	 benzoperoxoic acid	315	331	-5.3	298	5.2	376	-19.5
36	 3-chlorobenzoperoxoic acid	361	334	7.5	341	5.7	371	-2.7
37	 hexanebis(peroxoic acid)	390	347	11.0	364	6.7	388	0.4
38	 octaneperoxoic acid	304	308	-1.2	283	6.9	313	-2.9
39	 4-methylbenzoperoxoic acid	369	331	10.3	322	12.7	366	0.7
40	 2-carboperoxybenzoic acid	383	358	6.6	483	26.0	491	-28.1
41	 nonaneperoxoic acid	308	307	0.3	294	4.5	364	-18.1
42	 (*E*)-3-phenylprop-2-eneperoxoic acid	341	336	1.4	316	7.3	395	-16.0
43	 nonanebis(peroxoic acid)	363	345	5.0	397	9.5	417	-14.8
44	 decaneperoxoic acid	314	307	2.4	306	2.7	324	-3.1
45	 decanebis(peroxoic acid)	371	344	7.2	409	10.1	391	-5.3

Table 1 continued

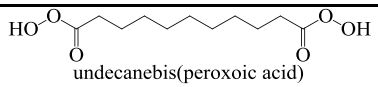
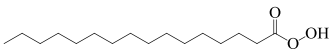
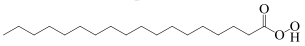
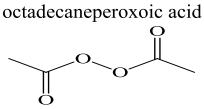
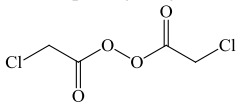
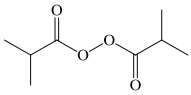
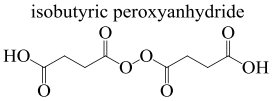
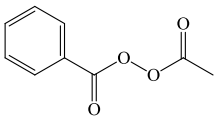
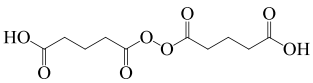
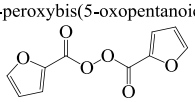
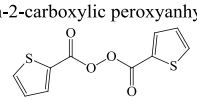
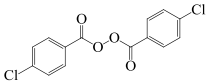
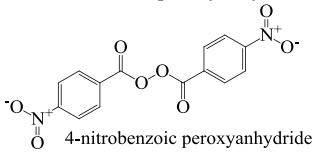
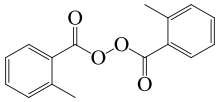
46	 undecanebis(peroxoic acid)	323	343	-6.2	431	33.5	392	-21.3
47	 1-hydroperoxytetradecane	329	304	7.5	351	6.5	340	-3.3
48	 hexadecaneperoxoic acid	334	303	9.3	373	11.7	346	-3.5
49	 octadecaneperoxoic acid	338	302	10.7	396	17.0	350	-3.5
50	 acetic peroxyanhydride	303	327	-7.7	220	27.6	344	-13.5
51	 2-chloroacetic peroxyanhydride	358	332	7.2	279	22.0	349	2.6
52	 isobutyric peroxyanhydride	353	324	8.3	235	33.6	301	14.8
53	 4,4'-peroxybis(4-oxobutanoic acid)	406	378	6.8	586	44.4	438	-8.0
54	 acetic benzoic peroxyanhydride	311	347	-11.4	302	2.9	366	-17.6
55	 5,5'-peroxybis(5-oxopentanoic acid)	377	377	0.0	608	61.3	433	-14.8
56	 furan-2-carboxylic peroxyanhydride	360	379	-5.3	399	10.8	407	-13.2
57	 thiophene-2-carboxylic peroxyanhydride	366	357	2.2	512	40.1	453	-23.9
58	 4-chlorobenzoic peroxyanhydride	411	372	9.3	470	14.4	436	-6.2
59	 4-nitrobenzoic peroxyanhydride	431	415	3.6	697	61.9	500	-16.1
60	 2-methylbenzoic peroxyanhydride	327	365	-11.7	433	32.2	477	-45.8

Table 1 continued

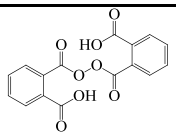
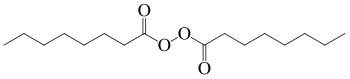
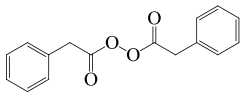
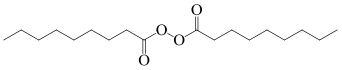
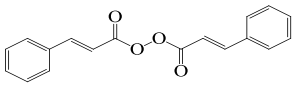
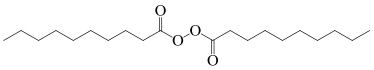
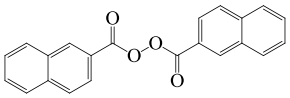
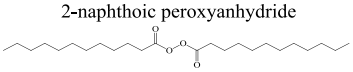
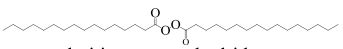
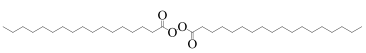
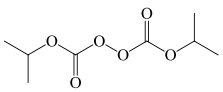
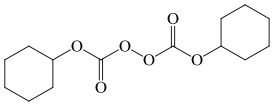
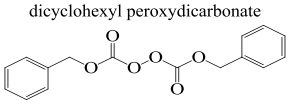
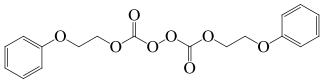
61	 2,2'-(peroxybis(carbonyl))dibenzoic acid	429	420	2.2	754	75.7	672	-56.6
62	 octanoic peroxyanhydride	302	320	-5.8	355	17.4	346	-14.5
63	 2-phenylacetic peroxyanhydride	314	365	-16.3	408	29.7	397	-26.4
64	 nonanoic peroxyanhydride	286	318	-11.2	377	31.7	350	-22.2
65	 cinnamic peroxyanhydride	407	376	7.6	420	3.3	552	-35.7
66	 decanoic peroxyanhydride	318	317	0.1	400	25.9	355	-11.8
67	 2-naphthoic peroxyanhydride	412	396	3.8	566	37.2	503	-22.0
68	 dodecanoic peroxyanhydride	328	315	4.0	445	35.6	361	-10.1
69	 palmitic peroxyanhydride	345	310	10.0	535	55.2	370	-7.3
70	 heptadecanoic stearic peroxyanhydride	350	308	12.0	580	65.8	373	-6.6
71	 diisopropyl peroxydicarbonate	282	293	-3.9	279	1.1	316	-12.0
72	 dicyclohexyl peroxydicarbonate	319	353	-10.8	391	22.6	608	-90.5
73	 dibenzyl peroxydicarbonate	375	387	-3.2	452	20.7	371	1.0
74	 bis(2-phenoxyethyl) peroxydicarbonate	372	407	-9.5	519	39.7	417	-12.2

Table 1 continued

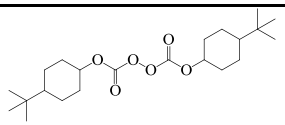
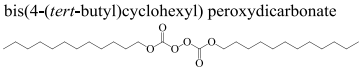
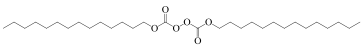
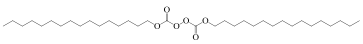
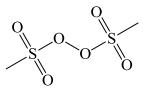
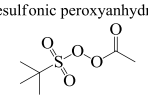
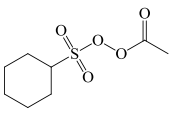
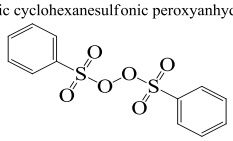
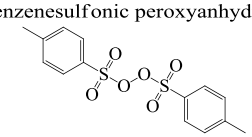
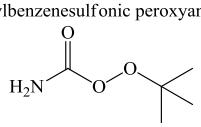
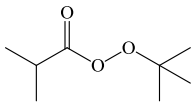
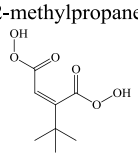
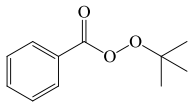
75	 bis(4-(*tert*-butyl)cyclohexyl) peroxydicarbonate	365	349	4.3	371	1.7	683	-87.3
76	 didodecyl peroxydicarbonate	302	335	-10.9	579	91.6	355	-17.5
77	 ditetradecyl peroxydicarbonate	314	333	-5.9	557	77.3	360	-14.6
78	 dihexadecyl peroxydicarbonate	325	330	-1.6	602	85.2	362	-11.3
79	 methanesulfonic peroxyanhydride	350	337	3.6	234	33.2	433	-23.7
80	 acetic 2-methylpropane-2-sulfonic peroxyanhydride	309	330	-6.8	249	19.6	448	-44.9
81	 acetic cyclohexanesulfonic peroxyanhydride	309	335	-8.5	290	5.9	545	-76.6
82	 benzenesulfonic peroxyanhydride	327	325	0.4	399	22.3	349	-6.8
83	 4-methylbenzenesulfonic peroxyanhydride	323	324	-0.3	447	38.3	370	-14.5
84	 *tert*-butyl carbamoperoxoate	324	307	5.4	296	8.6	418	-28.9
85	 *tert*-butyl 2-methylpropaneperoxoate	319	308	3.5	232	27.3	332	-4.1
86	 (*Z*)-2-(*tert*-butyl)but-2-enebis(peroxoic acid)	388	341	12.3	402	3.7	377	2.9
87	 *tert*-butyl benzoperoxoate	281	329	-17.0	307	9.2	420	-49.4

Table 1 continued

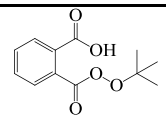
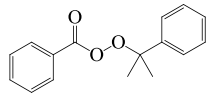
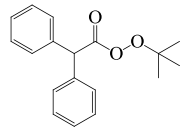
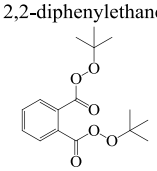
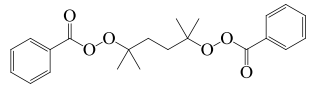
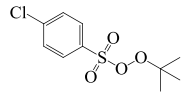
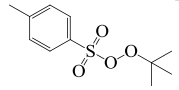
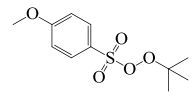
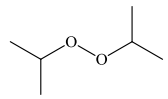
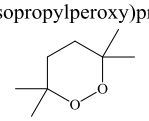
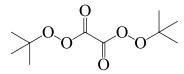
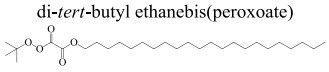
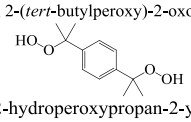
88	 2-((*tert*-butylperoxy)carbonyl)benzoic acid	377	355	5.8	492	30.2	560	-48.4
89	 2-phenylpropan-2-yl benzoperoxoate	318	349	-9.7	390	22.5	410	-28.9
90	 *tert*-butyl 2,2-diphenylethaneperoxoate	332	348	-4.7	397	19.6	380	-14.4
91	 di-*tert*-butyl benzene-1,2-bis(carboperoxoate)	330	364	-10.1	443	34.1	446	-35.0
92	 2,5-dimethylhexane-2,5-diyl dibenzoperoxoate	391	383	2.0	525	34.1	506	-29.4
93	 *tert*-butyl 4-chlorobenzenesulfonoperoxoate	306	337	-10.4	357	16.7	359	-17.5
94	 *tert*-butyl 4-methylbenzenesulfonoperoxoate	310	334	-7.8	338	9.1	356	-14.9
95	 *tert*-butyl 4-methoxybenzenesulfonoperoxoate	320	345	-7.6	360	12.5	424	-32.4
96	 2-(isopropylperoxy)propane	287	293	-1.9	172	40.2	139	51.6
97	 3,3,6,6-tetramethyl-1,2-dioxane	247	297	-20.2	257	3.8	371	-50.1
98	 di-*tert*-butyl ethanebis(peroxoate)	324	344	-6.2	336	3.8	433	-33.6
99	 docosyl 2-(*tert*-butylperoxy)-2-oxoacetate	315	323	-2.6	515	63.3	377	-19.6
100	 1,4-bis(2-hydroperoxypropan-2-yl)benzene	414	411	0.7	435	5.1	473	-14.3

Table 1 continued

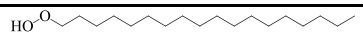
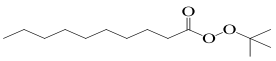
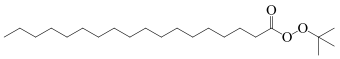
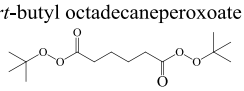
101	 1-hydroperoxyoctadecane	323	286	11.5	376	16.4	334	-3.5
102	 *tert*-butyl decaneperoxoate	267	304	-14.1	315	17.9	329	-23.4
103	 *tert*-butyl octadecaneperoxoate	312	300	4.0	405	29.6	374	-19.8
104	 di-*tert*-butyl hexanebis(peroxoate)	316	342	-8.3	382	20.9	194	38.5
	Average absolute deviation			6.8		24.1		25.4

Table 2 Standardized coefficients and some statistical parameters of molecular fragments and geometry factors of Eq. (2)

	Coefficients	Standard error	*p* value	Lower bound (95 %)	Upper bound (95 %)
Intercept	280.534	8.920239223	5.23826E−53	262.8319341	298.2357821
n_C	5.159	0.838101594	1.64428E−08	3.49568037	6.822050959
n_H	−2.870	0.411860774	3.71451E−10	−3.687803025	−2.053154465
n_O	10.651	1.800949203	4.88537E−08	7.077055967	14.22490595
$T^{+}_{m,peoroxide}$	38.897	6.94831263	1.97607E−07	25.10844906	52.68584891
$T^{-}_{m,peoroxide}$	−52.337	11.02235223	7.0093E−06	−74.21039849	−30.46340106

higher than experimental data. The presence of these groups may reduce the packing efficiency of molecules in the crystals, which can decrease the interaction between local dipole moments of neighboring polar groups. For the presence of only one –(CO)OO– or –O–C(O)–OO–(CO)–O– in form R_1–(CO)OO–R_1 or R_1–O–C(O)–OO–(CO)–O–R_1, the value of $T^{-}_{m,peoroxide}$ is 1.0 where R_1 in both side of organic molecule should be the same. The value of $T^{-}_{m,peoroxide}$ also equals 1.0 for R–C(O)OOH where the number of carbon atoms in R should contain less than five carbon atoms.

Statistical parameters and reliability of Eq. (2)

Table 2 shows statistical parameters of Eq. (2) corresponding to five variables of n_C, n_H, n_O, $T^{+}_{m,peoroxide}$ and $T^{-}_{m,peoroxide}$. It allows comparing the relative weight of the variables in the model. As indicated in Table 2, each of n_C, n_H, n_O, $T^{+}_{m,peoroxide}$ and $T^{-}_{m,peoroxide}$ has a highly significant impact as evidenced by their extremely small *p* values and standard errors. Standard error is a measure of the precision of evaluation of a coefficient in which precision can be measured by standard deviation over repeated measurements. Meanwhile, the *p* value measures the probability that a parameter estimated from experimental data should be as large as it is. For *p* value <0.05, the observed effect is not due to random variations and the effect is significant. Eq. (2) is a good correlation because its *R*-squared value or the coefficient of determination is 0.970 [40].

As indicated in Table 1, the predicted results of the new method for various peroxide compounds were also compared with JR [27] and JY [10] methods. The average absolute deviations of the new, JR [27] and JY [10] methods are 6.76, 24.14 and 25.42, respectively, which confirm high reliability of the new method with respect to both JR [27] and JY [10] methods. A visual comparison of the predicted results of the new, JR [27] and JY [10] methods with the experimental values is shown in Fig. 1. The predicted results of the new model show that it can be easily applied to molecular structures of different classes of peroxide compounds. Comparison of deviations of different classes of organic peroxides is given in Table 3. As seen, the best predictive result is related to peroxyacids, i.e., 5.9. For the other classes of organic peroxides, the proposed method can also provide good predictions because the difference between maximum and minimum of deviations is 1.8, which can be ignored.

Conclusions

A novel method has been developed for the simple and reliable prediction of melting points of hazardous peroxide

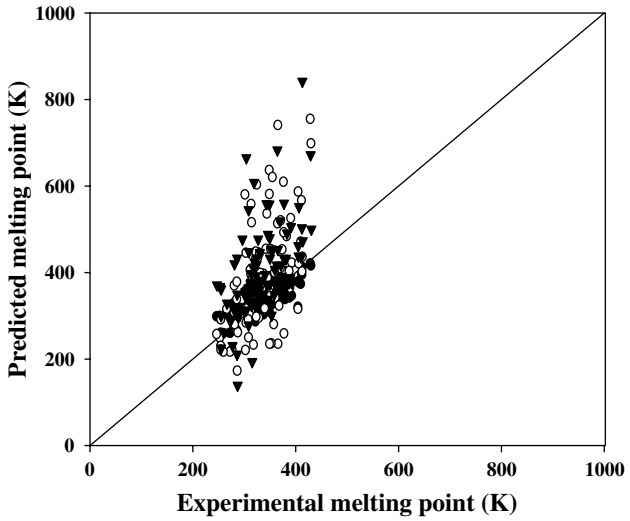


Fig. 1 Calculated melting points versus experimental data for different 104 peroxide compounds given in Table 1. The *solid lines* represent exact agreement between predictions and experiment. *Filled circle*, *hollow circle* and *filled triangle* denote the calculated values of the new, JR [27] and JY [10] methods, respectively

Table 3 Comparison of deviations of different classes of organic peroxide

Organic peroxide	Dev.
Hydroperoxides	6.1
Dialkyl peroxides	7.7
α-Oxygen substituted alkyl hydroperoxides and dialkyl peroxides	7.1
Primary and secondary ozonides	6.8
Peroxyacids	5.9
Diacyl peroxides	6.3
Alkyl peroxyesters	7.4

compounds including hydroperoxides, dialkyl peroxides, primary and secondary ozonides, peroxyacids, diacyl peroxides and alkyl peroxyesters compounds. The methodology presented here is based on a melting core temperature as well as $T^{+}_{\mathrm{m,peoroxide}}$ and $T^{-}_{\mathrm{m,peoroxide}}$ correction terms. As shown in Table 1, the new method gives more reliable predictions as compared to JR [27] and JY [10] methods, which may be taken as appropriate validation of the new method.

Since prediction of melting point of peroxide material is readily calculated in the new method by a desk calculator, the results of this study are appealing to chemists. The new model gives the simplest and easiest pathway for calculation of melting point of peroxide compounds. This reliable method confirms that the accuracy is not necessarily enhanced by greater complexity.

Acknowledgments We would like to thank the research committee of Kashan University for supporting this project.

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