Journal of Loss Prevention in the Process Industries 38 (2015) 254–259

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

journal homepage: www.elsevier.com/locate/jlp

A mathematical method for predicting heat of reaction of organic peroxides

L.L. Zhou, J.C. Jiang*, Y. Pan, Z.R. Wang

Jiangsu Key Laboratory of Hazardous Chemicals Safety and Control, College of Safety Science and Engineering, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Article history:
Received 19 June 2015
Received in revised form
30 August 2015
Accepted 27 September 2015
Available online 30 September 2015

Keywords:
Quantitative structure property relationship
Heat of reaction
Partial least squares
Applicability domain

ABSTRACT

The heat of reaction of organic peroxide is widely used to estimate the risk of fire and explosion in process industries. In this study, the quantitative relationship between the heat of reaction and the molecular structures of organic peroxides was established based on quantitative structure property relationship (QSPR). The genetic algorithm combined with partial least squares (PLS) was employed to select optimal subset of descriptors which had significant contribution to the overall heat of reaction. The best resulted model was consisted of seven variables which were Ss, Me, IVDM, HDcpx, ATS4m, MATS1e and MOR14m. Ss and Me are constitutional descriptors which are related to the electrical states of the atom, IVDM and HDcpx are topological descriptors which are related to the shape of the molecule, ATS4m and MATS1e are 2D autocorrelations descriptors which can reflect the topology structure of molecules and MOR14m is a 3D-MoRSE descriptor which can represent the spatial structure of the molecular. The correlation coefficient was 0.995 which mean the model had high fitting capacity. Model validation was also performed to check the stability and predictive capability of the presented model. The results showed that the presented model was a valid and predictive model. This study can provide a new way for predicting the heat of reaction of the organic peroxides.

1. Introduction

Organic peroxides have a characteristic of the bivalent —O—O— structure. The —O—O— bond trends to break and form free radicals of the form RO. Thus, organic peroxides have been widely employed in the chemical industry. That is, the molecular structures are not stable and very easy to collapse during accelerating exothermic decomposition (United Nations, 1998; Yoshida, 1993). Organic peroxides belong to active chemical substances that have certain energy themselves. In order to control this kind of reaction better, the heat release or the potential heat release of the chemical reaction should be characterized legitimately. And then the further assessment could be done, so could the protective measures.

The most common method representing thermal hazard is using the heat of reaction as a basis to judge, generally is the unit heat of reaction (ΔH) which is the formation heat between product and reactant per-mole. The greaterΔH, indicating that the more the heat emitted by the unit reactant, the more heat accumulation, and the greater risk of the reaction. In this study the heat of the complete combustion of organic peroxides was the research object. There have been some works about the thermal hazard of organic peroxide reported in past literatures (Fuyu et al., 2003; Joming et al., 2007; Lu et al., 2011). Most researchers obtained the data of reaction heat from experiments, and others gave results in the use of numeric methods. Among those numeric methods, the quantitative structure property relationship (QSPR) method has been proved to be effective to predict various physicochemical properties such as boiling point, melting point, flash point, vapor pressure, water solubility, critical properties and so on, which had been extensively reviewed elsewhere (Katritaky et al., 1995; Xidal, Rogers, Holste & Mannan, 2004; Katritaky and Fara, 2005; Patel et al., 2009; Katritaky et al., 2010; Pan et al., 2010; Reyes et al., 2011).

QSPR studies focus on the relationships between the properties of interest and the molecular structures of compounds which are expressed by a variety of molecular descriptors. The basic strategy of QSPR analysis is to find optimum quantitative relationships between molecular structure and physicochemical

* Corresponding author.
E-mail address: jcjiang@njtech.edu.cn (J.C. Jiang).

http://dx.doi.org/10.1016/j.jlp.2015.09.017
0950-4230/

properties, which can be used for the further prediction of physicochemical properties from only molecular structures. The advantage of this approach over other methods lies in the fact that it only requires the knowledge of chemical structure rather than dependence on experiments. Moreover, the molecular descriptors used in the QSPR models which are calculated from molecular structures have definite physicochemical information that has significant contribution to the targeted properties. In this study, QSPR method was applied to explore the quantitative relationship between the heat of reaction of organic peroxide and their molecular structures.

2. Materials and methods

2.1. Data set

For calculating the reaction heat, the formation heat of the substances referring in the reaction was necessary. In general, the formation heat could be measured with various calorimeters. However the measurement of unstable substances was difficult. The general theoretical methods for calculating reaction heat included the bond energy additive method, the group additive method, the semi-empirical molecular orbital method, the density functional theory and the ab initio method which was the first-principles method without any experimental parameters. In this paper the group additive method proposed by Benson was used to calculate the heat of formation. The calculation of this method is easy for the formation heat of gaseous phase and the result precision can meet the requirement of risk prediction. Previous studies showed that the formation heat of gaseous phase could replace the solid and the liquid in risk prediction (Yoshida, 1989). The values of formation heat of the different groups used in this paper were showed in Table 1.

According to the data in Table 1, the formation heat of the various substances can be calculated. For a complete combustion reaction the combustion heat could be obtained by the sum of products formation heat subtracting the sum of reactant formation heat. In the complete combustion the product is CO_2 and H_2O. The formation heat of CO_2 is 393.71 kJ/mol and H_2O is 241.84 kJ/mol.

The dataset for this study was composed of 57 organic peroxides which were chosen from the List of Dangerous Chemicals 2015 and randomly divided into a training set (48) and a testing set (9). The reaction heat of 57 organic peroxides were calculated on the basis of the mentioned method.

2.2. Determination of molecular descriptors

To obtain a QSPR model, compounds must be represented by a variety of molecular descriptors including constitutional, topological, geometrical, and electrostatic, which have been extensively reviewed elsewhere (Karelson et al., 1996; Todeschini and Consonni, 2000). It is the primary in the QSPR studies to determine various molecular descriptors as overall as possible. In this paper, many descriptors relating to the bonds length and bonds angles were optimized on the basis of the minimum energy molecular geometries optimized by the HyperChem software (version 7.5, HyperChem is copyrighted by Hypercube, Inc) based on MM + molecular mechanics force field and AM1 semiempirical method. And then the Dragon program (version 5.4, DRAGON is copyrighted TALETE srl) which was an efficient program for the calculation of molecular descriptors was used to calculate the molecular descriptors which were used to search for the best QSPR model of the heat of reaction (Todeschini et al., 2006). In all, a total of 1167 descriptors were calculated for each compounds in the data set. The detailed description on the types of the descriptors that Dragon can calculate and the calculation procedure of the descriptors can be found in Dragon software user's guide (Todeschini et al., 2006).

After the calculation of molecular descriptors, an initial analysis was performed to remove some of them to reduce the size of the model development and to keep relevant descriptors only. Considering that some descriptors cannot encode the structural differences between compounds that accounts for their different ΔH_C values, the descriptors that stayed constant and near constant for all molecular were removed from the descriptor pool. Moreover, pairwise correlations between descriptors were also examined for further reducing the descriptor pool, and only one descriptor was retained from a pair contributing similar information (correlation coefficient >0.96 in this study). These reductions resulted in a reduced pool of 523 descriptors for further study.

2.3. Descriptor selection and model development

Among these 523 descriptors calculated and selected through the information of the structures, there were many duplicate descriptors or descriptors which were not useful for modeling. Therefore, it was very important to select optimal subset of descriptors which had significant contribution to the desired property.

Table 1
The values of formation heat of the different groups.

Group	Heat of formation (kcal/mol)	Group	Heat of formation (kcal/mol)
C–(H)$_3$(C)	−11.58	C–(H)$_2$C$_2$	−6.11
C–(H)(C)$_3$	−3.28	C–(C)$_4$	−1.33
C–(C)$_3$(O)	−21.12	C–(C)$_2$(O)$_2$	−31.74
O–(O)(C)	10.04	O–(O)(H)	−11.48
C$_B$–(O)	−20.00	C$_B$–(CO)	−20.35
C$_B$–(H)	1.95	C$_B$–(C)	3.14
CO–(O)(C)	−54.15	CO–(H)(C)	−35.88
CO–(H)(C$_B$)	−10.00	CO–(C$_B$)(O)	−29.79
CO–(H)(O)	−50.00	CO–(O)$_2$	−87.50
O–(O)(CO)	−4.19	O–(C)(CO)	−14.17
O–(H)(CO)	−51.60	C–(H)$_2$(O)(C)	−24.84
C–(H)(O)(C)$_2$	−22.86	C–(H)$_2$(O)$_2$	24.78
C–(H)$_2$(O)(C$_B$)	−18.16	C–(H)$_2$(C)(C$_B$)	−4.28
C–(CO)(H)$_3$	−10.00	C–(C)$_2$(H)(CO)	−0.75
C–(CO)(H)$_2$(C)	−5.48	C–(C$_B$)(H)$_3$	−10.00
C$_d$–(H)(C)	7.00	C$_d$–(H)(CO)	−10.87
CO–(C$_d$)(O)	−33.0	Cyclohexane	−0.73
C–(CO)(C)$_3$	5.45		