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Self-accelerating decomposition temperature and quantitative structure–property relationship of organic peroxides

Yanjie Gao[a], *Yan Xue*[a,b], *Zhi-guo Lǚ*[a,*], *Ziheng Wang*[a], *Qiang Chen*[a], *Ning Shi*[b], *Feng Sun*[b]

[a] *College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*
[b] *State Key Laboratory of Chemicals Safety & Control, Qingdao 266071, China*

ABSTRACT

This work presents a new approach to predict thermal stability of organic peroxides based on quantitative structure–property relationship methods. The data set consists of self-accelerating decomposition temperature (SADT) of 39 organic peroxides, part of which is obtained from the Recommendations on the Transport of Dangerous Goods and the other part is obtained from C600 calorimetry. Descriptors computed using RM1 semi-empirical quantum mechanical method are selected to describe the above-mentioned 39 molecules. Partial least-squares method and multiple linear regression method are used to select the descriptors and SADT model. At last, a four-descriptor correlation equation is obtained using a cross validation method: a correlation coefficient $R > 0.9$ and a predictive coefficient $Q^2 > 0.85$.

Keywords: Organic peroxide; Self-accelerating decomposition temperature; Quantitative structure–property relationship; Multi-linear regression; modeling; thermal decomposition; kinetics parameters; material thermal hazard

1. Introduction

Organic peroxides are widely used in many industrial fields such as synthetic resin, synthetic rubber, resin modifying agent and oxidant for organic synthesis. Recent years, with rapid development of chemical industry and extensive exploitation of fine chemicals, some new organic peroxides and peroxide intermediates have appeared. But organic peroxides are unstable organic compounds containing peroxide functional group (R—O—O—R′) in which the oxygen–oxygen bond is weak. So even under low temperature, they can decompose and produce free radicals which can result in self-accelerating reaction, or even lead to runaway reactions when the heat released is not removed efficiently. In 1990, an explosion took place abruptly in the production process of benzyl peroxide in Japan, resulting in a severe accident in which 9 persons died and 17 persons injured (Zhang et al., 2004; Lei, 2003; Kao and Hu, 2002). Therefore, the extensive research of hazard evaluation of organic peroxides has important theoretical and practical significance.

There are many characters to illustrate the hazard of organic peroxide, such as onset temperature, heat of decomposition, total adiabatic temperature rise, time to maximum rate, and self-accelerating decomposition temperature (SADT) (He, 2008; Gang et al., 2007). Above all, SADT is an important parameter that characterizes thermal hazard under transport conditions of self-reactive substances (Kossoy and Sheinman, 2007). According to the United Nations "Recommendation on the Transport of Dangerous Goods (TDG), Manual of Tests and Criteria", the definition of SADT is: the lowest temperature at which self-accelerating decomposition may occur with a

* *Corresponding author*. Tel.: +86 532 84022719.
E-mail address: lvzhiguo@qust.edu.cn (Z.-g. Lǚ).

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substance in the packaging as used in transport. The Globally Harmonized System had also inherited the SADT as a classification criterion for self-reactive substances (GHS, 2003). But only few SADTs of organic peroxides listed in the TDG is not enough for industrial process and transportation in the quickly developed modern life, so it is necessary to develop a convenient and quick method to evaluate the SADT of new organic peroxide.

The TDG recommends four tests to determine the SADT: The United States SADT test (US SADT test), adiabatic storage test, isothermal storage test and heat accumulation storage test (Dewar test). But all of the four tests have serious disadvantages in performing process. It is time-consuming, expensive and dangerous. To overcome these disadvantages, some quick and easy methods were developed. In the 1990s, methods for determination of SADTs using kinetic data obtained by accelerating rate calorimeter, vent sizing package, or adiabatic heat velocity response calorimeter were developed, and the predicted results were in agreement with the literature values (Wilberforce, 1981; Fisher and Goetz, 1993; Mores et al., 1994; Yu and Hasegawa, 1996; Yang et al., 2003). Less sample size, less danger and more time-saving are the advantages of this method compared with TDG method. Following problems must be considered in evaluating SADTs of organic peroxides: Firstly, organic peroxide is a large group with hundreds of members. Secondly, great variations of hazards characters were observed among different types of organic peroxides (Duh et al., 2008; Noller et al., 1964; Mohan et al., 1982). So it will be very time consuming and very expensive to evaluate SADT of every organic peroxide.

The quantitative structure–property relationship (QSPR) method is a new way to solve above-mentioned problems. Since 1980s, QSPR has always been the hot article in the basic research, especially in the field of drug design (Taskinen and Yliruusi, 2003). QSPR is a versatile tool used to study the relationship between chemical or physical properties of substances and molecule structure, and to predict chemical or physical properties of unknown or non-existent substance, based on models that derived from quantitative analysis between chemical or physical properties and inner molecule structures. It is generally operated as following: to find structure descriptors which can exactly describe current molecular structure; and using appropriate statistical modeling tools to build a quantitative model based on analysis between properties and molecule structure. Once reliable model is established, it can be used to predict chemical or physical properties of molecules (Yansheng et al., 2009).

Morrill and Byrd (2008) and Fayet et al. (2009) studied energetic materials such as nitro-aromatic compounds, and established QSPR model with a satisfying predicting result. Lu et al. (2011) studied 16 organic peroxides, and derived two QSPR models to predict onset temperature (T_o) and heat of decomposition (Q_d), both of them had good predictive ability. But there are only 16 samples in their data sets which cover little part of organic peroxide groups, and the descriptors included in the model are too many and complicated, e.g., 13 descriptors are used in the model to predict T_o. T_o and Q_d are also not commonly used in industrial and transportation processes. In this work, SADTs of 38 organic peroxides were studied, and a QSPR model for predicting SADT is derived using partial least-squares method).

2. QSPR methodology

2.1. Experimental apparatus and steps

C600 trace heat meter (Setaram Co., France) was used for the experiments.

AKTS (Advanced Thermal Analysis Software, version 3.19) and FEA (finite element analysis) were used in the calculation of SADTs.

The test samples and a thermal inertia material (such as Al_2O_3) as reference were put in two sample pool and heated at the same time in order to measure the relative change of the heat flow beam. It was the same as differential scanning calorimeters in principle, yet its sample container (standard sample tank volume 12.5 m^3) can be equipped with mixing, stirring, gas flow and so on to meet the different need, e.g., atmospheric pressure, high pressure, or vacuum conditions, gas circulation flow, dumping type, film type or liquid filter type used to measure specific heat of liquid, liquid and gas heat transfer rate. So it is very useful in the safety evaluation. C600 trace heat meter is mainly composed of the following several parts: the reactor, controller, power box and operation of the instrument computer software platform.

Specific experimental and data treatment procedures are as follows:

(1) 0.2 g or so sample is added in a clean C600 sample pool and the lid of the sample pool is covered and screwed up.
(2) The sample cell and reference pool is joined into test borehole.
(3) The temperature program (temperature range from room temperature to 300 °C, heating rate, respectively, is 0.1 °C/min, 0.5 °C/min and 1 °C/min) is set, and the experiment begins.
(4) After the experiment, the temperature has dropped to room temperature, the sample pool can be removed, cleaned and dried.

The SADTs of the organic peroxides obtained by Semenov model form the calorimetric curves are as follows:

(1) The relationship between extent of reaction and temperature is obtained by analysis and calculation of the calorimetric curves.
(2) Activation energy and pre-exponential factor are established by data processing using Friedman method.
(3) SADTs are gained by FEA method using AKTS.

2.2. QSPR methodology

QSPR is used to consistent relationships between the molecular structures and the chemical or physical properties for a series of compounds in the chemical or biological fields so that these “rules” can be used to predict unknown properties of new chemicals.

A QSPR model generally takes the form of a linear equation:

$$\text{Property} = f(\text{structure descriptors}) + \text{error}$$

Usually, QSPR modeling is a stepwise process consisting of five main steps: