J Therm Anal Calorim (2012) 107:943–948
DOI 10.1007/s10973-011-1536-3

Study on thermal properties and kinetics of benzoyl peroxide by ARC and C80 methods

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Received: 2 March 2011 / Accepted: 23 March 2011 / Published online: 9 April 2011

Abstract Benzoyl peroxide (BPO) has been widely used in the industrial and food field, it is sensitive to shock, heat and friction, and causes thermal explosion incidents easily. Therefore, it is important to understand its thermal behaviors and kinetics for loss prevention and safety management. Two kinds of experimental methods (C80 calorimetry and accelerating rate calorimetry) were used to study the hazardous characteristics of BPO, and idea kinetic parameters, such as the pre-exponential factor and the activation energy were obtained. These results contribute to improve the safety in the reaction, transportation, and storage processes and help to the stability criterion of decomposition reaction of BPO.

Keywords Benzoyl peroxide (BPO) · Kinetics · C80 calorimetry · Accelerating rate calorimetry (ARC) · Thermal behaviors

Abbreviations

Φ	Thermal inertia
M_s	Mass of the sample
M_b	Mass of the bomb
M_0	Initial mass of reactant
M_T	Mass of reactant at time t
$C_{p,s}$	Heat capacity of the sample (kJ/kg K)
$C_{p,b}$	Heat capacity of the bomb (kJ/kg K)
x	Conversion rate (%)
A	Pre-exponential factor of Arrhenius equation (s^{-1})
E_a	Activation energy (kJ/mol)
ΔH	Reaction heat of unit reactant (kJ/mol)
t	Reaction time (min)
T	Temperature of system at time t (K)
$T_{o,s}$	Onset exothermic temperature
T_f	Maximum temperature (K)
ΔT_{ad}	Adiabatic temperature rise (K)
$m_{o,s}$	Self-heating rate at $T_{o,s}$
$m_{m,s}$	Maximum self-heating rate
n	Reaction order
k	Constant of reaction rate
R	Gas constant (8.31415 J/mol K)
dH/dt	Overall heat flow (W)
dT/dt	Self-heat rate (K/s)

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Introduction

Benzoyl peroxide (BPO) is a nontoxic, colorless, and odorless dangerous chemical material [1, 2], which is widely used in the field of food and industry. Dry BPO is a crystalline solid and usually contains less than 5% water. Wet BPO contains between 50–85% BPO and 15–50% water. BPO is relatively steady at normal temperature, but it is flammable under dry condition and is sensitive to shock, heat, and friction etc. This is because there is a single oxygen–oxygen (O–O) bonding in the molecule chains of BPO, and the O–O bondings break easily and cause decomposition reaction. The thermal explosion incidents caused by BPO in the world were summarized in the previous study [3, 4]. A major explosion accident which killed 9 people, injured 49 people, and destroyed 7 buildings took place in 1990 in a Japanese BPO production

plant. Another explosion accident happened in a food additives plant in Zhengzhou city of Henan province, China, resulting in 27 deaths, 33 wounded, and 500,000 US$ loss in 1993. Therefore, it has been regarded as a fatal chemical.

Chemical reactions of BPO are often associated with thermal runaway [5, 6] when the heat release in a reaction exceeds the heat transfer into the surroundings. This case makes the temperature of the reaction system rise, and furthermore, it increases the reaction rate of BPO and accelerates heat accumulation. This is because the reaction rate, as well as the rate of heat generation can be increased exponentially, while the heat loss rate to the surroundings increased linearly with temperature. As a result, the heat accumulation and the reaction temperature increase, and a runaway reaction developed ultimately. In order to evaluate the thermal hazard of BPO, an in-depth understanding of thermal behaviors and kinetics of BPO is necessary, and there are less literature for the thermal kinetics of BPO with ARC and C80 calorimetry method have been reported.

In this study, various theoretical techniques and small-scale tests were taken to provide data on the likelihood and risk of a thermal runaway reaction, and the thermal hazard analysis of full-size plant was simulated by ARC and C80 calorimetry tests.

Experimental

Material

The BPO (99% purity industrial products) was supplied from Hengtai Chemical Co. Ltd., China, and not treated before used. Its density was 1.32 g/cm^3.

C80 and ARC apparatus

The C80 microcalorimeter is a heat-flow calorimeter (Setaram, France) used to determine the heat flux produced from samples under isotherm or scanning mode. It has the reputation of high sensitivity, a quite wide testing temperature range from room temperature to 300 °C and many other functions. The thermal effects of each sample with temperature under 0.1 μg mass were recorded easily. C80 is connected to a data acquisition and control unit, as well as to a computer equipped with the SETSOFT software, which can be used to calculate thermodynamics and kinetic data. The schematic diagram of C80 calorimeter is shown in Fig. 1.

The ARC is one of the important tools for evaluating the chemical thermal risk, reaction temperature, and heat change throughout the reaction time; it is also one of the most sensitive tools for the thermal stability evaluation.

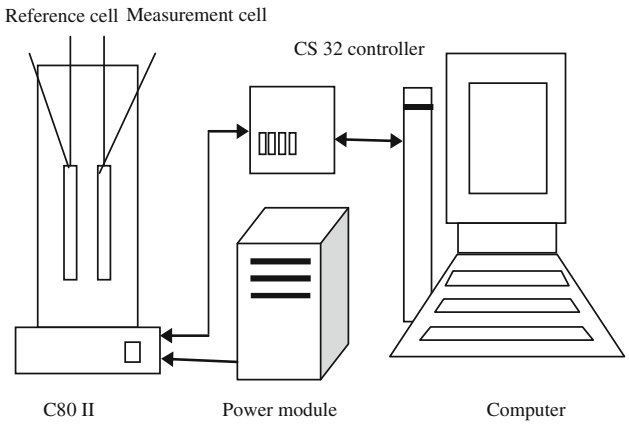


Fig. 1 Schematic diagram of C80 calorimeter

ARC method is designed specifically to study thermal decomposition and other exothermic reactions on a small scale in a closed cell, providing a dynamic adiabatic environment in which the reaction can auto-accelerate. Figure 2 shows the "heat-wait-search" operation mode of ARC. After heating the sample, the instrument waits for a certain amount of time to allow the system to build thermal equilibrium and starts to search for exothermic process. If no exothermic process is detected, the instrument continues heating-searching operation. If an exothermic process is detected, then the instrument starts to track this exothermic process.

Results and discussion

Thermal properties of BPO

Organic peroxides have organic (or carbon-containing) groups attached to the molecular chain at one side of the

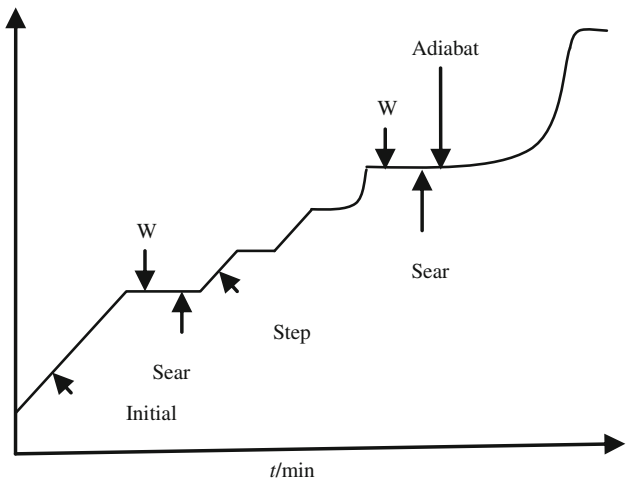


Fig. 2 The 'heat-wait-search' operation mode of ARC

oxygen–oxygen bonding. Their thermal instability is caused by the weak oxygen–oxygen bonding, which leads to a tendency toward more stable substances. Although their potential unit energy is low compared to that of conventional explosives, these compounds can be very destructive when the stored energy is released. The thermal decomposition of peroxides is comprised of two main elements [7, 8]:

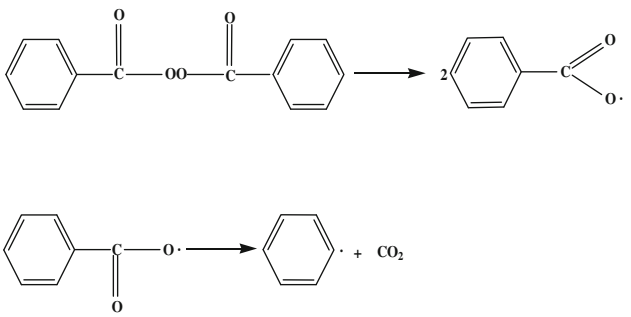
(1) Homolysis of the O–O bonding

$$[(RCO_2)]_2 \rightarrow \ 2RC(O) - O$$

(2) Radical-induced decomposition

$$[(RCO_2)]_2 + R' \rightarrow \ R - C(O) - O - R' + RC(O) - O.$$

It is not easy to determine the contribution of each decomposition mode in the overall process for any peroxide. Generally speaking, the decomposition reaction mechanism of BPO can be expressed as below.



The final degradation products of BPO are carbon dioxide and biphenyl, and also smaller amount of phenyl benzoate and benzene are produced.

C80 calorimetry measurement

In the experiment of C80, 0.1990 g BPO was placed in the measurement cell, and the same weight of Al_2O_3 was placed in the reference cell. The sample was heated at a 0.1 °C min^{-1} heating rate from room temperature to 300 °C. Figure 3 shows the C80 heat-flow curve of BPO at a 0.1 °C min^{-1} heating rate from room temperature to 200 °C.

It can be shown from Fig. 3 that the heat flow increased sharply above 90.1 °C. In other words, BPO started to release heat at 90.1 °C and the exothermic peak was at 95.4 °C with the reaction heat of −219.3 kJ mol^{-1}. The reaction curve initially rose and then went down after reaching a maximum. The reason can be explained as

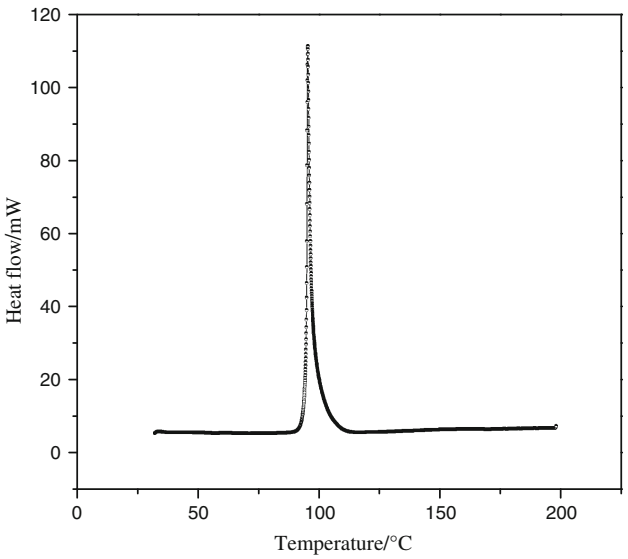


Fig. 3 C80 heat-flow curve of BPO

follows: at each constant temperature, an intermediate free radical was generated and thus caused the reaction rate to rise, as well as the heat flow increased gradually until reaching the climax. During this stage, the concentration of the intermediate free radical was rising, though its generation and consumption were simultaneously happening all the time. After reached the climax, the consumption of the free radical tended to be dominant and the heat flow decreased with the time.

ARC measurement

The reaction temperature, self-heating rate, and pressure data may be collected during the exothermic processes with ARC. It is effective to get the relationship between the adiabatic temperature rise, self-heating data, time, or temperature from the experimental data. It is also convenient to determine full kinetic and thermodynamic information from the results [8].

In the ARC experiment, 1.9970 g BPO was placed in a spherical sample bomb, and then the sample bomb was positioned inside the calorimeter. The standard ARC mode of "heat-wait-search" was used. According to the properties of BPO, the set starting temperature of ARC was 60 °C and the end-point temperature was 400 °C. The temperature of the system was raised from the starting temperature in 5 °C steps at a heating rate of 0.02 °C min^{-1}.

In the experiment, temperature versus time curve of BPO is shown in Fig. 4 and self-heating rate versus temperature curve of BPO is shown in Fig. 5.

It can be known from Figs. 4 and 5 that the exothermic reaction of BPO had not taken place at 60 °C, and by

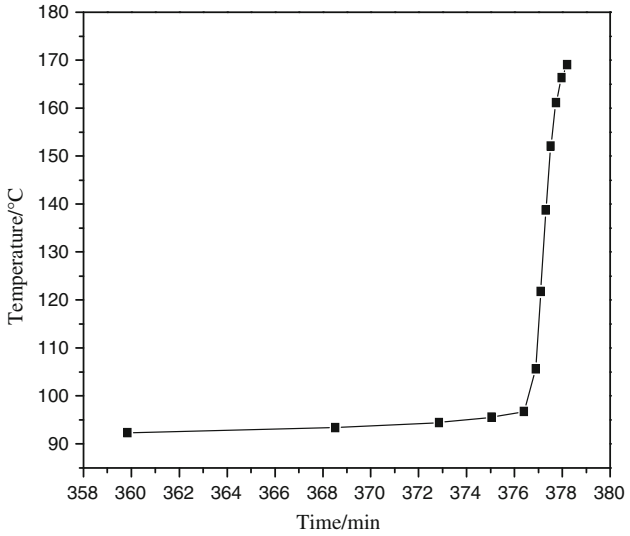


Fig. 4 Temperature versus time curve of BPO

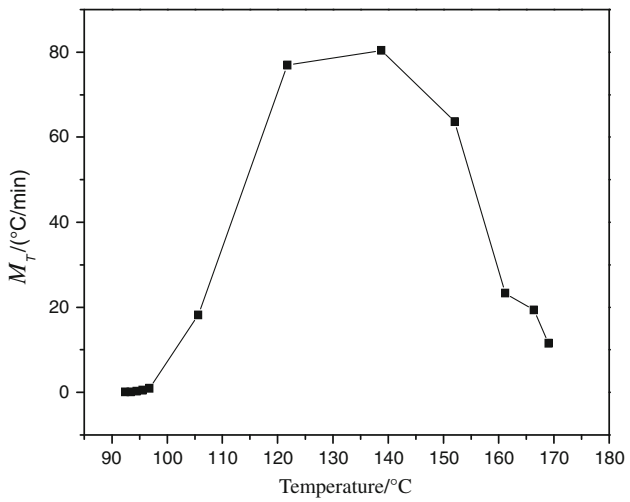


Fig. 5 Self-heating rate versus temperature curve of BPO

several "heat-wait-search" periods, ARC detected an exothermic reaction at 92.39 °C (self-heating rate was 0.11 °C min^{-1} at this temperature, and it was greater than the set heating rate of 0.02 °C min^{-1}). That was to say, 92.39 °C was the starting exothermic temperature for reaction system. When the temperature reached to 96.79 °C, there was a sharp temperature rise. At 138.75 °C, the reaction system had the maximum self-heating rate of 80.38 °C min^{-1}, and then the self-heating rate began to decline. But the temperature of reaction system continued to rise, and ultimately reached to the highest value of 169.03 °C. The thermal characteristic parameters of BPO obtained by ARC experiment are shown in Table 1.

Table 1 Thermal characteristic parameters of BPO obtained by ARC

$T_{o,s}$/°C	$m_{o,s}$/°C min^{-1}	$T_{f,s}$/°C	$\Delta T_{ad,s}$/°C	$m_{m,s}$/°C min^{-1}
92.39	0.11	169.03	76.64	80.38

$T_{o,s}$ onset exothermic temperature; $m_{o,s}$ self-heating rate at $T_{o,s}$; $T_{f,s}$ maximum temperature; $\Delta T_{ad,s}$ adiabatic temperature rise; and $m_{m,s}$ maximum self-heating rate

The decomposition heat released from the sample was not only used for heating itself, but also for heating the bomb, so there was some heat loss. This heat loss is known as the thermal inertia and is reliable based on the simple correction of the apparatus. The thermal inertia is known as Φ and quantified as the Φ correction [9].

$$\Phi = 1 + \frac{M_b C_{p,b}}{M_s C_{p,s}}, \tag{1}$$

where M_s and M_b are the mass of the sample and the bomb, $C_{p,s}$ and $C_{p,b}$ are the heat capacity of the sample and the bomb, respectively. The thermal characteristic parameters of BPO modified by Φ are shown in Table 2.

Kinetics study of BPO

Kinetics calculation by C80 method [9–11]

According to the Arrhenius law, the rate of chemical reaction can be expressed in the following formula.

$$\frac{dx}{dt} = A\exp(-E_a/RT)(1-x)^n, \tag{2}$$

where x is the conversion rate and $x = (M_0 - M)/M_0$; M_0 is the initial mass of reactant; M is the mass of reactant at time t.

Substituting x into Eq. 2, the Eq. 3 can be obtained:

$$-\frac{dM}{dt} = M_0 A\exp(-E_a/RT)\left(\frac{M}{M_0}\right)^n. \tag{3}$$

If the reaction heat of unit reactant is ΔH, the expression of the heat release rate can be defined as Eq. 4 [11, 12]:

$$\frac{dH}{dt} = \Delta H M_0 A\exp(-E_a/RT)\left(\frac{M}{M_0}\right)^n. \tag{4}$$

At initial stage of the reaction, the reactant consumption should be negligible (generally below 2%). Therefore, M may approximately be equal to M_0, and Eq. 4 is simplified as Eq. 5:

Table 2 Thermal characteristic parameters of BPO modified by Φ

Φ	T_o/°C	M_0/°C min^{-1}	T_f/°C	ΔT_{ad}/°C
2.58	92.39	0.28	290.12	197.73

$$\frac{dH/dt}{\Delta H M_0} = A\exp(-E_a/RT). \quad (5)$$

Taking natural logarithm of Eq. 5, the Eq. 6 is got:

$$\ln\left(\frac{dH/dt}{\Delta H M_0}\right) = \ln A - \frac{E_a}{R}\cdot\frac{1}{T}. \quad (6)$$

By plotting the curve of $\ln[(dH/dt)/(\Delta H\cdot M_0)]$ versus $1/T$, the activation energy (E_a) and pre-exponential factor (A) can be easily calculated (in Fig. 6). The data in Fig. 6 gives calculated value of E_a and A are 104.36 kJ mol^{-1} and 3.28 $\times$ 10^{10} s^{-1}, respectively.

Kinetics calculated by ARC method [2, 13]

Reaction kinetics of the sample can be determined from the experimental data obtained by ARC experiment. According to the heating rate Eq. 7 [14–16], the Eq. 8 can be easily obtained.

$$M_T = \Delta T_{ad} k\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n \quad (7)$$

$$k = \frac{M_T}{\Delta T_{ad}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} \quad (8)$$

The natural logarithm pattern of the Arrhenius law is described as Eq. 9. Then combining the Eqs. 8 and 9, the Eq. 10 is obtained.

$$\ln k = \ln A - \frac{E_a}{R}\cdot\frac{1}{T} \quad (9)$$

$$\ln\frac{M_T}{\Delta T_{ad}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n} = \ln A - \frac{E_a}{R}\cdot\frac{1}{T} \quad (10)$$

Assuming the decomposition reaction of BPO is the first-order reaction and $n = 1$, then Eq. 10 can be simplified as Eq. 11.

$$\ln\frac{M_T}{T_f - T} = \ln A - \frac{E_a}{R}\cdot\frac{1}{T} \quad (11)$$

By plotting the curve of $\ln[M_T/(T_f - T)]$ versus $1/T$ (see Fig. 7), the activation energy can be calculated from the slope of the line, and the pre-exponential factor can be calculated from the ordinate at the origin of it. The calculated value of the activation energy and pre-exponential factor of BPO are E_a = 152.80 kJ mol^{-1}, A = 3.61 $\times$ 10^{19} s^{-1}, respectively.

The onset temperature of BPO detected by C80 method is 90.1 °C, while by ARC method, it is 92.39 °C. For the thermal hazard materials or systems, as the decomposition provides the necessary excited energy at lower temperature, the thermal property data is critical to its thermal runaway. At this point, C80 has advantage over ARC method clearly. Furthermore, the reaction heat can be obtained by integrating the peak of the C80 heat-flow curve, and here the reaction heat of BPO was −219.3 kJ mol^{-1}.

The kinetics parameters of BPO got by the C80 and ARC method have little difference. The ARC parameter is larger than that from C80 data. According to literature [2], the value of activation energy and pre-exponential factor of BPO are E_a = 112.70 kJ mol^{-1}, A = 9.20 $\times$ 10^{12} s^{-1}, respectively, in the initial stage of decomposition reaction. The results obtained from C80 data (E_a = 104.36 kJ mol^{-1}, A = 3.28 $\times$ 10^{10} s^{-1}) are much closer to the reference value (E_a = 112.70 kJ mol^{-1}, A = 9.20 $\times$

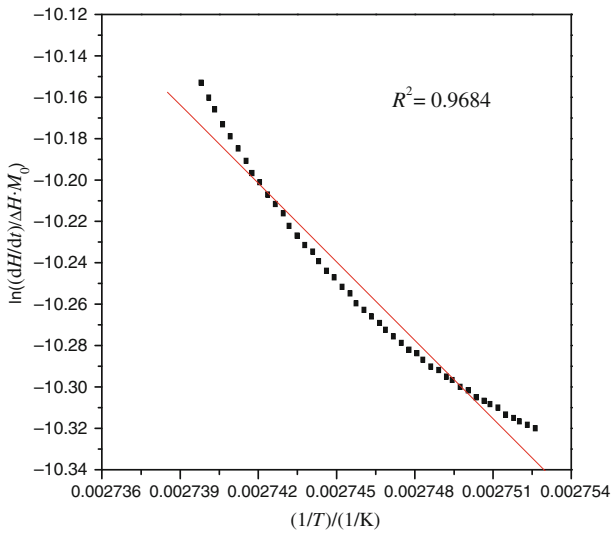


Fig. 6 $\ln[(dH/dt)/(\Delta H\cdot M_0)]$ versus $1/T$ of BPO

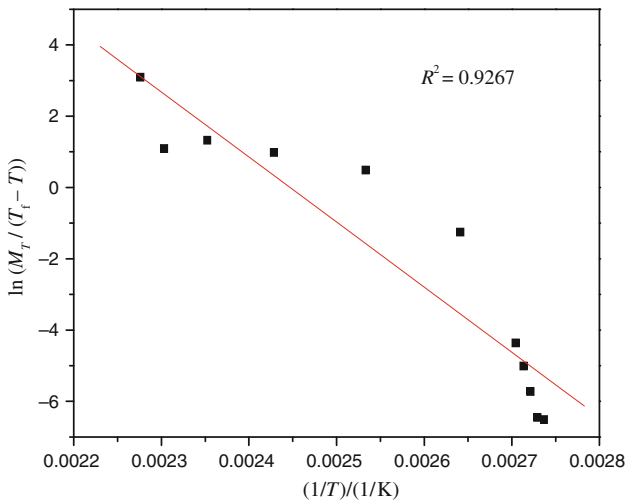


Fig. 7 $\ln[M_T/(T_f - T)]$ versus $1/T$ of BPO

10^{12} s^{-1}). While the results obtained from ARC data ($E_a = 152.80$ kJ mol^{-1}, $A = 3.61 \times 10^{19}$ s^{-1}) deviate from the reference value. In addition, from the fitted straight line in Figs. 6 and 7, it can be seen that the deviation from the C80 result is smaller than that of ARC. This indicates that more reliable result can be obtained from C80 data. It should be noted that the variation around the linear drawn in the plots of $\ln[M_T/(T_f - T)]$ versus $1/T$ and $\ln[(dH/dt)/(\Delta H \cdot M_o)]$ versus $1/T$ are systematic and not random, which indicates that the chemical reaction was apparently fit to the Arrhenius law.

Safety management suggestion of BPO

The hazardous characteristics of BPO were investigated and discussed in this study. The results show that a number of important recommendations for safe handling, storage, and manufacture about BPO are necessary:

(1) There is a single oxygen–oxygen (O–O) bonding easy to brake in the BPO molecule. It makes BPO sensitive to shock, heat, and friction, so safeguards should be taken to protect against the possibility of its exposure to ignition sources, friction, and shock etc. [17, 18]. In addition, equipments used to process BPO should be isolated from the storage area of BPO, other equipments, and work areas. Electrical equipment should be adequately grounded and explosion-proof.
(2) The experiment results with ARC and C80 methods show that BPO decomposes around 90 °C, so safeguards and steps should be taken place to avoid BPO overheating or contamination which may initiate the decomposition reaction.
(3) Decomposition reaction of BPO can generate a large amount of gas [2, 16], so workshop and warehouse of BPO should be built with blast walls with adequate capabilities to vent pressure.

Conclusions

Decomposition reaction of the BPO resulted in heat release, which may lead to thermal runaway with gas, fire, and explosion formation, therefore, an in-depth understanding of thermal behavior and kinetics of BPO is important for loss prevention and safety management. In this study, ARC and C80 calorimetry technologies were used for evaluating the thermal hazards of BPO. Both of the technologies showed good performance in the research of the thermal properties and kinetics parameters of BPO. The calculated values of activation energy and pre-exponential factor are $E_a = 152.80$ kJ mol^{-1}, $A = 3.61 \times 10^{19}$ s^{-1} and $E_a = 104.36$ kJ mol^{-1}, $A = 3.28 \times 10^{10}$ s^{-1} by ARC and C80 data, respectively. Furthermore, it is speculated that the C80 data could obtain more reliable kinetic parameters of BPO than ARC method.

Acknowledgements This research was supported by Sinopec Safety Engineering Institute, Qingdao, China and State Key Laboratory of Safety and Control for Hazardous Chemicals, Qingdao, China. The authors are also thankful to the Natural Science Foundation of Shandong Province (Grant No. ZR2010BL022) and the Qingdao Science Foundation (Grant No. 8-1-3-17-jch), China.

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