J Therm Anal Calorim (2012) 109:975–980
DOI 10.1007/s10973-011-1789-x

Thermal hazard evaluation of tert-butyl peroxide using non-isothermal and adiabatic calorimetric approaches

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Received: 12 June 2011 / Accepted: 4 July 2011

Abstract Tert-butyl peroxide (TBPO), is a typical organic peroxides (OPs),which is widely applied as initiator in poly-glycidyl methacrylate (PGMA) reaction, and is employed to provide a free-radical in frontal polymerization, and which has also caused many thermal runaway reactions and explosions worldwide. To find an unknown and insufficient hazard information for an energetic material, differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2) were employed to detect the fundamental thermokinetic parameters involving the exothermic onset temperature (T_0), heat of decomposition (ΔH_d), temperature rise rate ($dT \cdot dt^{-1}$), time to maximum rate under adiabatic situation (TMR_{ad}), pressure rise rate ($dP \cdot dt^{-1}$), and maximum pressure (P_{max}), etc. The T_0 was calculated to be 130 °C using DSC and VSP2. Activation energy (E_a) of TBPO was evaluated to be 136 kJ mol^{-1} by VSP2. In view of the loss prevention, calorimetric applications and model evaluation to integrate thermal hazard development are adequate means for inherently safer design.

Keywords Differential scanning calorimetry (DSC) · Heat of decomposition (ΔH_d) · Organic peroxides (OPs) · Tert-butyl peroxide (TBPO) · Vent sizing package 2 (VSP2)

List of symbols

A	Frequency factor, s^{-1} M^{1-n}
C_p	Liquid specific heat at constant pressure, kJ kg^{-1} °C^{-1}
C_0	Initial concentration, mol L^{-1}
E_a	Activation energy, kJ mol^{-1}
K	Pre-exponential factor, s^{-1}
M	Mass of reactant, g
P_{max}	Maximum pressure during overall reaction, psig
Q	Calorific capacity, J g^{-1}
$\dot{Q}$	Heat flow, W g^{-1}
R	Gas constant, 8.314 J mol^{-1} K^{-1}
S	Wetted surface area, m^2
SADT	Self-accelerating decomposition temperature, °C
T	Temperature, °C
T_A	Final adjusted temperature, K
T_{A0}	Initial adjusted temperature, K
T_f	Final temperature, °C
T_M	Final measured temperature, K
T_{max}	Maximum temperature during overall reaction, °C
T_{M0}	Initial measured temperature, K
T_{NR}	Temperature of no return, °C
T_{wall}	Temperature on the wall, °C
TMR_{ad}	Time to maximum rate under adiabatic system, min, h
U	Heat transfer coefficient, kJ min^{-1} m^{-2} K^{-1}

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a	Vessel wetted surface area, m^2
k_i	Rate at stage i, s^{-1}
m	Mass of reactor, kg
n	Order of reaction, dimensionless
α	Degree of conversion, dimensionless
β	Heating rate, °C min^{-1}
λ	Heat conductivity, J ms K^{-1}
ϕ	Thermal inertia, dimensionless
ΔH_d	Heat of decomposition, J g^{-1}
$(dT \cdot dt^{-1})$	Self-heating rate, °C min^{-1}
$(dT \cdot dt^{-1})_A$	Actual self-heating rate, °C min^{-1}

Introduction

Thermal runaway reaction and explosion accidents have been studied and discussed in recent years. In fact, the heat generation rate (Q_g) exceeding the heat removal rate (Q_r) in a reactor is called runaway reaction by Semenov theory [1, 2]. In addition, when the Q_g is equal to Q_r (heat accumulation ($Q_{acc.}$) = 0) under lower reaction temperature, then that is defined as a stable situation. Therefore, from the above basic concept, it is understood that it is unstable in such system under high temperature because Q_r is less than Q_g. The operator should avoid the reaction occurring under high temperature.

Tert-butyl peroxide (TBPO), which is one of the organic peroxides (OPs), is a violent exothermic chemical. Therefore, OPs are widely investigated and studied in Korea, China, Japan, and Taiwan. Many studies indicate that the peroxy group (–O–O–) of OPs is one of the reasons for its exothermic nature [3–5]. To prevent thermal runaway reaction and thermal explosion incidents, the process engineers have to carefully consider the thermodynamics and thermokinetics involved in a reactive system.

TBPO is widely applied as an initiator in poly-glycidyl methacrylate (PGMA) reaction [6], and is employed to provide free-radical in frontal polymerization [7]. In the past, using differential scanning calorimetry (DSC) and vent scanning package 2 (VSP2), calorimetric approaches for analyzing the crucial thermokinetic parameters of OPs have been proposed by a couple of excellent studies over the latest years [8–12]. This study was used to survey the fundamental thermal hazard of TBPO. The exothermic onset temperature (T_0), heat of decomposition (ΔH_d), activation energy (E_a), frequency factor (A), maximum temperature (T_{max}), temperature rise rate ($dT \cdot dt^{-1}$), time to maximum rate under adiabatic situation (TMR$_{ad}$), pressure rise rate ($dP \cdot dt^{-1}$), and maximum pressure (P_{max}), etc., were adopted to analyze, and to solve safety problem in chemical industries or polymerization process with safety approach. In addition, DSC is an easy operating calorimeter that was used to calculate and determine thermal behavior, and useful parameters including T_0, ΔH_d, and T_{max}.

According to the thermal curves by DSC tests, the T_0 was calculated to be 110–130 °C. Process engineers and operators must control the temperature of a reactor less than T_0 (110 °C). To prevent thermal accumulation, the temperature of the cooling system must also be kept at low temperature circumstance in a reactor.

Experimental

Samples

Ninety-eight mass% TBPO was directly purchased from the Fluka Co., and both density and concentration were measured. Then, TBPO was stored in a refrigerator at 4 °C. Ninety-eight mass% TBPO was utilized to evaluate thermal hazard by DSC. To prevent and evaluate thermal explosion of TBPO, 20 mass% TBPO (in 80 mass% toluene), 25 mass% TBPO (in 75 mass% toluene), 30 mass% TBPO (in 70 mass% toluene), and 98 mass% TBPO were used to detect thermal behavior of TBPO by adiabatic calorimeter.

Differential scanning calorimetry (DSC)

Dynamic scanning experiments were performed on a Mettler TA8000 system coupled with a DSC 821e measuring test crucible (Mettler ME-26732) that could withstand relatively high pressure of about 100 bar. STARe software was employed for acquiring thermal curves. For the sake of a better thermal equilibrium, a variety of heating rates (β) were chosen, such as 2, 4, 6, and 10 °C min^{-1}. About 1–10 mg of the sample was selected for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler DSC, and we conducted dynamic scanning by starting the programed setting [13–16].

The T_0 calculation method development using isothermal and heating model by DSC

Generally speaking, the baseline analysis approach was chosen to calculate the T_0 of material by DSC with heating model in tradition method. The T_0 determination depending on the thermal curve in the tradition method has higher variance than the new approach in this study. To evaluate the T_0 of TBPO, DSC was applied to two ways that were described as follows:

- First, the DSC was employed to test the thermal behavior under various isothermal temperatures from 90 to 130 °C holding for 10 h by isothermal model of DSC. To fit the process situation, this test was selected for temperatures from 90 to 130 °C by DSC with isothermal circumstance.
- Second, the same crucible after isothermal temperature holding for 10 h was used to evaluate the thermal hazard of TBPO under 4 °C min^{-1} of heating rate (from 30 to 300 °C). Then, the T_0 can be determined by two ways in this new approach.

Vent sizing package 2 (VSP2)

VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske & Associates, Inc., was utilized to obtain thermokinetic and thermal hazard data, such as temperature and pressure traces versus time. The low heat capacity of the cell ensured that in all the reaction, the heat released remained within the tested sample. Thermokinetic and pressure behavior in the same test cell (112 mL), usually, could be tested without any difficult extrapolation to the process scale due to the low thermal inertia factor of about 1.05–1.32. Information available from the VSP2 test includes [17, 18]:

- Heat of reaction (ΔH).
- Total adiabatic temperature rise (ΔT_{ad}).
- Adiabatic kinetics parameters (1st order).
- Rates of temperature and pressure rise ($\mathrm{d}T \cdot \mathrm{d}t^{-1}$ and $\mathrm{d}P \cdot \mathrm{d}t^{-1}$).
- Reaction onset temperature (T_0).
- System vapor pressure versus temperature.
- Adiabatic time to maximum rate (TMR_{ad}).
- Maximum temperature ($T_{\max}$) and pressure ($P_{\max}$).
- Two-phase flow regime.
- Temperature of no return (T_{NR}).
- Resident incubation time to decomposition.

E_a and A evaluation with adiabatic calorimeter

The kinetic parameters of a single reaction can be evaluated from the equations derived by Townsend and Tou [19] for an adiabatic process:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

$$\ln k = \ln \frac{\frac{\mathrm{d}T}{\mathrm{d}t}}{C_0^{n-1}\left(\frac{T_f - T}{T_f - T_0}\right)^n (T_f - T_0)} \tag{2}$$

where the rate constant is represented by Arrhenius law:

$$k = Ae^{-\frac{E_a}{RT}} \tag{3}$$

Substituting the experimental thermal data from VSP2 into Eq. 2, and assuming that $n = 1$, we can plot ln k versus $-1000/T$ and obtain a very good straight line. The A and E_a for adiabatic reaction are summarized in Table 3.

The VSP2 operational technologies

The experiment of VSP2 is difficult and dangerous because a thermal explosion and runaway reaction exists, when the pressure generation rate is increasing quickly. Operators must take careful note of the information of the sample including the basic exothermic circumstance, physical conditions, and thermal hazard parameters…etc. Figures 1a and b display thermal hazard for the VSP2 testing. If the exothermic reaction of the sample is high, the system could be damaged by pressure generation. The test cell and the thermocouple damage by runaway reaction are shown in Fig. 1a. High pressure generation in test cell over the system capacity will cause an explosion of the P_1 (pressure transducer) that is shown in Fig. 1b.

This study could apply plenty of technologies for loss prevention of damage control in the VSP2 experiment shown as follows:

- The volume of the sample is limited to be 50 mL (112 mL of test cell).

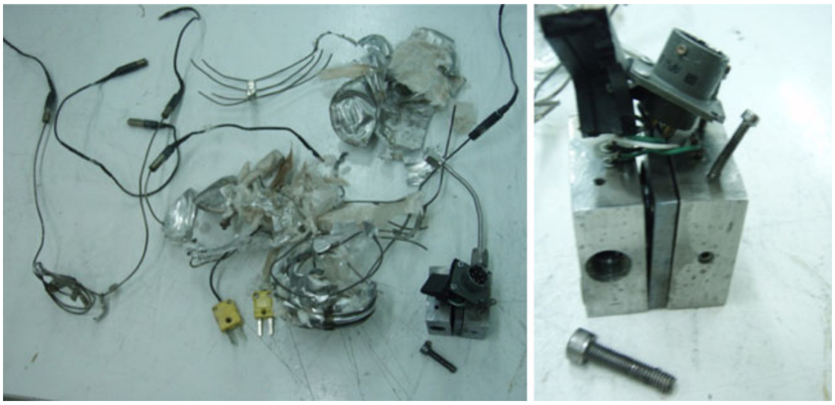

Fig. 1 Pressure explosion of experiment using the VSP2. **a** Damage of heater. **b** Damage of pressure transducer

- The experiment of low concentration chemical (less than 20 mass% of sample) is handled first (especially for the OPs).
- If the experiment must be handled to use a high concentration of material, the operator must reduce the volume of the sample (less than 10 mL).
- The pressure valve must be opened when the experiment starts.
- If the operator meets an emergency condition, the window of ventilation system must be turned off and the experiment field evacuated.
- The volume of N_2 must be checked when the experiment gets started.

Results and discussion

Thermal analyses of TBPO using non-isothermal calorimetry

TBPO was included in OPs group. Ninety-eight mass% TBPO was applied to evaluate its thermal hazard by DSC under four heating rates. Ninety-eight mass% TBPO decomposed the ΔH_d about 1,200 J g^{-1}. The T_0 of ninety-eight mass% TBPO was determined at 120 °C (Table 1). The E_a, A, n, and so on were used to simulate the thermal explosion or runaway reaction by a reactor for chemical engineering applications. This study was applied to develop a new method for the T_0 determination. Ninety-eight mass% TBPO was applied to test the thermal decomposition behavior by using isothermal model of DSC under 90–130 °C holding for 10 h, respectively. Second, this study did not take out the sample crucible and did the scanning experiment under 4 °C min^{-1} of heating rate (temperature range is 30–300 °C) by DSC. The aim of this study was analyzed, as to whether the material was catalyzed to decompose by temperature.

The T_0 of 98 mass% TBPO was indicated to be 90 °C. According to Fig. 2, the peak of non-isothermal test is higher than the experiment under 90 °C of isothermal test. Therefore, the true T_0 was identified to be 80 °C (Table 2). In fact, the environmental temperature at 90 °C can catalyze the TBPO decomposition.

Table 1 Safety parameters of TBPO under various heating rates by DSC tests

β/°C min^{-1}	Mass/mg	T_0/°C	ΔH_d/J g^{-1}	T_{max}/°C	n
2	3.4	120	1,198	170	1
4	4.4	122	1,140	178	1
6	3.2	126	933	185	1
10	4.6	132	850	190	1

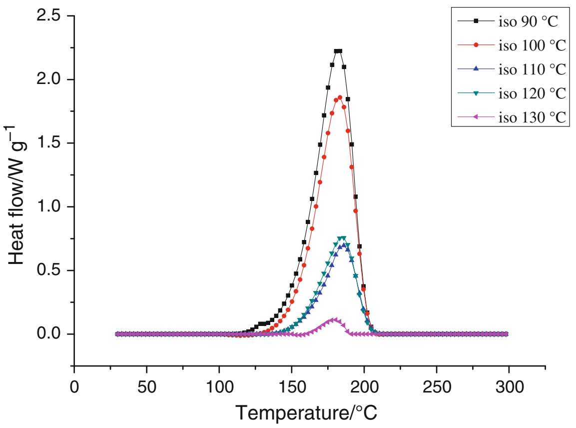

Fig. 2 Thermal behavior determination of 98 mass% TBPO by DSC isothermal-heating method

Table 2 The ΔH_d of 98 mass% TBPO calculation after isothermal temperature using 4 °C of heating rate by DSC

Isothermal temperature/°C	Mass/mg	T_0/°C	ΔH_d/J g^{-1}	T_{max}/°C
90	3.1	152	1,073	182
100	3.1	153	871	182
110	4.2	161	291	185
120	3.7	156	320	185
130	5.7	163	28	180

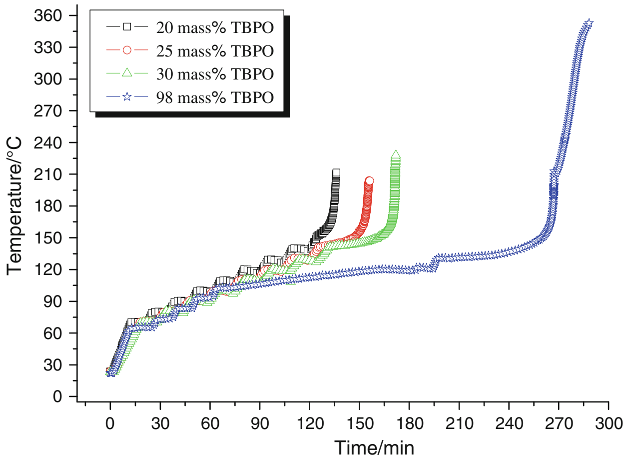

Fig. 3 Temperature vs. time for thermal decomposition of 20, 25, 30, and 98 mass% TBPO by VSP2

Runaway reaction evaluation by adiabatic calorimetry (using VSP2)

The T_0 of 20, 25, 30, and 98 mass% TBPO by VSP2 were calculated to be 150, 145, 140, and 120 °C (Fig. 3). Five mL of 98 mass% TBPO was used to assess thermal hazard by VSP2. A few amount of 98 mass% TBPO can be

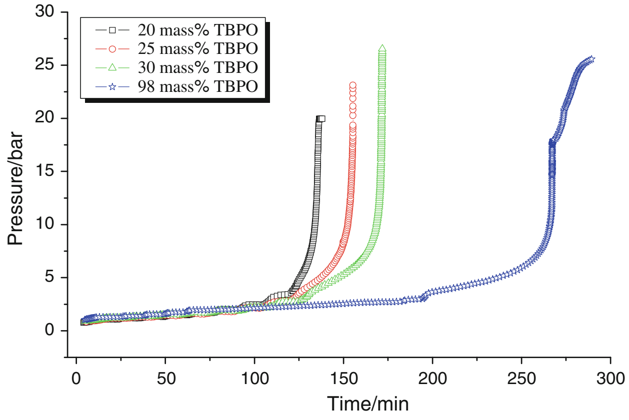

Fig. 4 Pressure vs. time for thermal decomposition of 20, 25, 30, and 98 mass% TBPO by VSP2

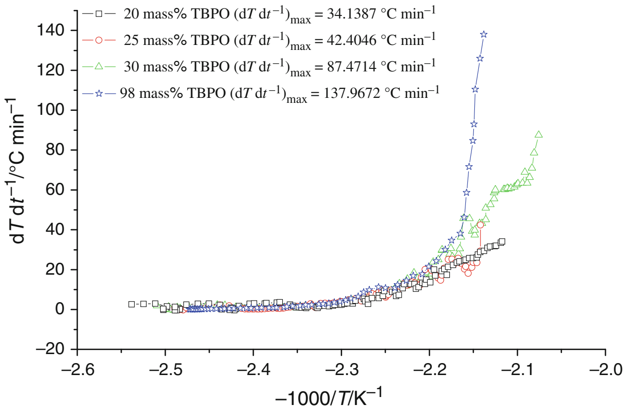

Fig. 5 Self-heating rate ($dT \cdot dt^{-1}$) on temperature from VSP2 experimental data for 20, 25, 30, and 98 mass% TBPO

detected as highly hazardous in its character. The T_{max} of 30 mass% TBPO is higher than that of 20 mass% (in Fig. 3). The P_{max} of 20 mass% TBPO was determined to be 19 bar by VSP2. The P_{max} of 25 mass% TBPO was calculated to be 23 bar using VSP2. The P_{max} of 30 mass% TBPO was analyzed to be 26 bar (Fig. 4). The P_{max} of 98 mass% TBPO was assessed to be 25 bar (Fig. 4). Figures 5 and 6 show the $dT \cdot dt^{-1}$ and the $dP \cdot dt^{-1}$ of 20, 25, 30, and 98 mass% TBPO. Substituting the experimental thermal data from VSP2 into Eq. 2, and assuming that $n = 1$,

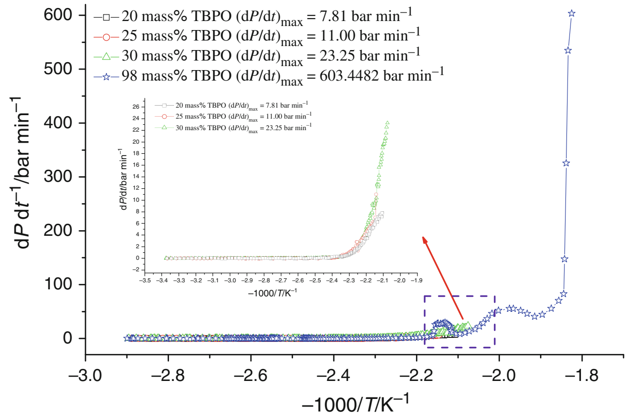

Fig. 6 Dependence of pressure rise rate ($dP \cdot dt^{-1}$) on temperature from VSP2 experimental data for 20, 25, 30, and 98 mass% TBPO

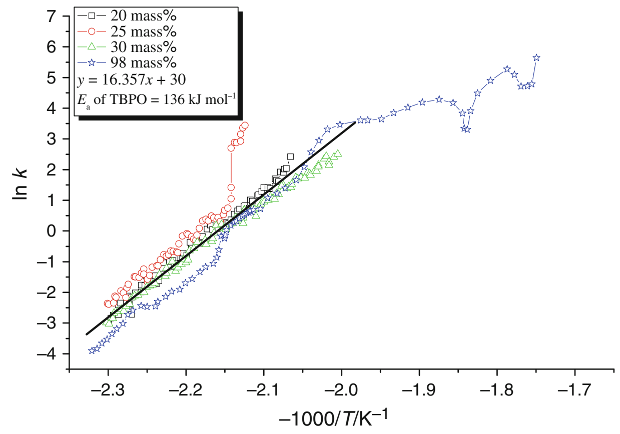

Fig. 7 The correlation of overall rate constant (k) and temperature (T) for 20, 25, 30, and 98 mass% TBPO by VSP2

we can plot ln k versus $-1000/T$, and obtain a very good straight line as in Fig. 7. The estimated kinetic parameters A and E_a for adiabatic reaction are summarized in Table 3. Ea of TBPO was calculated to be 136 kJ mol^{-1} (Table 3). TMR_{ad} of 98 mass% TBPO was calculated to be 70 min for emergency response time. High TBPO concentration (98 mass% TBPO) is more dangerous than the lower one. This study was employed to suggest that low TBPO

Table 3 Thermokinetics of 20, 25, 30, and 98 mass% TBPO by VSP2 tests

Conc./mass%	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT \cdot dt^{-1})_{max}$/ °C min^{-1}	$(dP \cdot dt^{-1})_{max}$/ bar min^{-1}	ΔT_{ad}/°C	TMR_{ad}/min	Φ	E_a/kJ mol^{-1}
20 (30 mL)	150	211	20	35	8	61	15	1.1	136
25 (30 mL)	140	203	23	42	11	63	25	1.1	136
30 (30 mL)	135	227	26	87	23	92	35	1.1	136
98 (5 mL)	120	350	25	137	603	230	70	1.2	136

concentration should be applied for use, storage, and transportation.

Conclusions

TBPO, one of the OPs, is a dangerous material for process safety engineer use in the manufacturing system. Loss prevention and damage control of OPs are compartmentalized into two parts: runaway reaction prevention, and incident occurrence for emergency response for an incident occurring. In this study, the E_a of TBPO was about 136 kJ mol^{-1}. In view of the loss prevention, calorimetric applications combined with model analysis for integrating thermal hazard development are mandatory, and are useful for fire fighters during perturbed conditions. According to all thermal curves by DSC tests, the T_0 was calculated to be 110–130 °C. Process engineers and operators must control the temperature of a reactor less than T_0 (110 °C). To prevent thermal accumulation, the temperature of the cooling system must also be kept at low temperature circumstance in a reactor. TMR$_{ad}$ of 98 mass% TBPO was calculated to be 70 min for emergency response time. High TBPO concentration (98 mass% TBPO) is more dangerous than the lower one. This study was employed to suggest that low TBPO concentration should be applied for use, storage, and transportation.

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