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Thermal hazard evaluation of the autocatalytic reaction of benzoyl peroxide using DSC and TAM III

Shang-Hao Liu [a], Hung-Yi Hou [b], Chi-Min Shu [c,*]

[a] Doctoral Program, Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology (YunTech), 123, University Rd., Sec. 3, Douliou, Yunlin 64002, Taiwan, ROC
[b] Department of Occupational Safety and Health, Jen-Teh Junior College of Medicine, Nursing and Management, 1, Jen-Teh Rd., Houlong, Miaoli 35665, Taiwan, ROC
[c] Department of Safety, Health, and Environmental Engineering, YunTech, Douliou, Yunlin 64002, Taiwan, ROC

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ABSTRACT

A new approach was used to monitor the autocatalytic reaction of benzoyl peroxide (BPO) by non-isothermal and isothermal kinetic models constructed using differential scanning calorimetry and thermal activity monitor III analyses, respectively. Autocatalytic reactions generally start slowly and then accelerate as the reactant is consumed and the autocatalyst is produced. Consequently, an autocatalytic reaction may require special design considerations to avoid certain upset conditions, such as runaway exothermic reactions.

We conducted a thermal hazard analysis of various products, including benzoic acid, benzene, and phenol, which were deliberately selected and individually mixed with BPO to investigate their thermal hazards. Model fitting can be applied to predict the amount of time required to achieve the maximum rate under isothermal conditions at any temperature of interest. The proposed procedure was effective and accurate for evaluating the autocatalytic reaction of BPO.

1. Introduction

From the viewpoint of process loss prevention, a global effort is underway to decrease the thermal hazards of chemical catastrophes. Table 1 lists a number of selected disasters that have resulted from high-risk compounds in several countries [1–4]. Particular attention is given to several explosions from the thermal runaway of organic peroxide (OPs) induced by external fires or other perturbed situations [5]. During thermal evaluation, non-isothermal and isothermal conditions are commonly applied by various calorimetric technologies. One important factor for assessing thermal risk is the identification of a runaway reaction.

In autocatalytic reactions, the product of a reaction acts as a catalyst and promotes the subsequent conversion of the reactant to the product [6,7]. Generally, this type of reaction initially has a slow reaction rate that accelerates as the reactant is consumed and the auto-catalyst is produced. Under certain conditions, autocatalytic reactions may require special design considerations, including the potential for thermal runaway [6,7].

The simplest autocatalytic system involves two steps, as shown in Eq. (1) through Eq. (3).

$$A \rightarrow B \tag{1}$$

$$A + (n-1)B \rightarrow nB \tag{2}$$

$$B \rightarrow C \tag{3}$$

where n is the order of the autocatalytic system. When n is equal to 2, the system is quadratic, and when n is equal to 3, the system is cubic. The first step is required to initiate the overall reaction, and it is generally much slower than the second autocatalytic step [6–8].

Benzoyl peroxide (BPO), a compound that is classified in the organic peroxide group, is widely used to initiate polymerization and as a bleaching reagent [9]. Overall, BPO is a non-toxic, colorless, odorless, and tasteless crystalline solid that is very thermally unstable and readily degrades to form benzoic acid, carbon dioxide, carbon monoxide, benzene, biphenyl, and terphenyl, which are the typical products of BPO in solution via a free-radical mechanism, as shown in Fig. 1 [10]. On May 26, 1990, an explosion and fire occurred when packaging a high-concentration

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[*] Corresponding author. Tel.:+886 5 534 2601x4416; fax: +886 5 531 2069.
E-mail address: shucm@yuntech.edu.tw (C.-M. Shu).

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Nomenclature

A	Pre-exponential factor (1/s)
C_v	Specific heat capacity (J/g °C)
E_a	Apparent activation energy (kJ/mol)
n	Molar number (dimensionless)
q	Heat generation rate at temperature T (°C/min)
R	Gas constant (J/mol K)
T	Temperature of sample (K)
T_f	Final temperature (°C)
T_0	Apparent exothermic onset temperature (°C)
T_p	Peak temperature (°C)
TMR_{iso}	Time to maximum rate under isothermal conditions (h)
W_p	Highest heat flow at time t (W/g)
ΔH	Enthalpy change (J/g)
ΔH_d	Heat of decomposition (J/g)

product at a BPO manufacturing plant in Japan. The entire plant was destroyed, multiple residential units in the neighborhood were damaged, and nine employees died [5,11]. Therefore, theoretical studies regarding autocatalytic reactions are concerned with unique exothermic features via specific calorimetry.

Wang et al. initially observed the autocatalytic reaction of BPO and obtained the exothermic behavior, BPO mixed with benzoic acid, via thermal activity monitor III (TAM III) [12]. To emphasize safety concerns, the purpose of our study was further to focus on the thermal behaviors of BPO for autocatalytic reaction when individually mixed with the self-products, such as benzene, benzoic acid, or phenol and predict the maximum rate under isothermal conditions (TMR_{iso}) at any temperature by model fitting. We used differential scanning calorimetry (DSC) to determine the fundamental thermokinetic data and the essential safety parameters, such as the apparent exothermic onset temperature (T_0), peak temperature (T_p), final temperature (T_f), and heat of decomposition ($\triangle H_d$), which were obtained by calorimetry [3,13]. These results will be useful for setting up the experimental design under isothermal conditions.

TAM III analysis was used to detect decomposition phenomena during storage and transportation under isothermal conditions. This type of analysis has been applied extensively to evaluate incompatible reactions for thermokinetic data, such as the time required to reach TMR_{iso}, highest heat flow (W_p), and reaction time [14]. Generally, the parameters provide process loss prevention information for BPO used in the manufacturing process and help us establish emergency relief systems under upset situations.

2. Experimental and method

2.1. Samples

Benzoic acid (98 mass%) and BPO (75 mass%) in the form of white crystalline solid substances were procured from PRS Panreac (Milano, Italy) and Aldrich (Missouri, USA), respectively. Benzene (95 mass%), a limpid liquid, was obtained from Alfa Aesar (Lancashire, UK), and phenol (97 mass%), a transparent crystalline solid substance, was purchased from Aldrich. These chemicals were stored in a refrigerator at 4 °C. Several experimental techniques, including preliminary estimates, DSC and TAM III, were conducted as described previously [15–17].

2.2. Differential scanning calorimetry (DSC)

Dynamic scanning experiments were performed using a Mettler TA8000 system coupled with a DSC 821^e measuring test crucible (Mettler ME-26732), which is an essential component of this experiment. This system was used for carrying out experiments involving relatively high pressures of up to 100 bar. The STAR^e software was used to obtain thermal curves for analysis [17,18]. The scanning rate selected for the temperature programmed ramp was 4 °C/min. The range of temperature increase was between 30 and 300 °C for BPO, benzene, benzoic acid, and phenol. Approximately 5 mg of the samples, which were mixed with 2.5 mg of the products, was hermetically sealed in the test

Table 1
Selected thermal explosion accidents since 1990 [1–4].

Date	Location	Chemicals	Injuries	Fatalities	Cause
1990.05.26	Japan	BPO	17	9	Thermal decomposition
1992.02.29	USA	Phenolic resins	4	0	Thermal decomposition
1994.08.18	USA	Phenolic resins	0	0	Cooling failure
1996.10.07	Taiwan	MEPKO	47	10	Thermal decomposition
1997.09.10	USA	Phenolic resins	4	1	Thermal decomposition
1999.02.23	USA	Naphtha	1	4	Fire (leaking)
1999.03.24	Taiwan	DCPO	0	0	Fire
2000.08.24	Korea	OPs	1	0	Thermal decomposition (dryer)
2003.01.02	USA	OPs	11	3	Unknown (storage tank)
2010.08.01	Taiwan	OPs	0	0	Thermal explosion (storage tank)
2010.04.04	Taiwan	Cyclohexane	0	0	Fire (reactor)
2010.06.11	Taiwan	Xylene	5	2	Thermal explosion (storage tank)
2010.07.07	Taiwan	Propylene	0	0	Fire (ethylene plant pipeline)
2010.12.30	Taiwan	Formic acid	2	0	Incompatibility explosion (storage tank)
201103.29	Taiwan	Naphtha	0	0	Fire (naphtha cracker plant's pipeline gas leak)
2011.04.05	Taiwan	Acrylonitrile	3	1	Toxic chemicals leaking (chemical tank)
2011.05.11	Taiwan	LPG	0	0	Fire (pipeline gas leak)
2011.07.26	Taiwan	Hydrogen	0	0	Fire (pipeline gas leak)
2011.07.30	Taiwan	Propylene	0	0	Explosion (refinery)
2012.02.01	Taiwan	Petroleum	0	0	Fire (RDS[a])
2012.04.06	Taiwan	Butadiene	0	0	Fire (pipeline leak)
2014.07.31	Taiwan	Propylene	310	30	Explosion (pipeline leak)

[a] Residual hydrodesulfurization unit.