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Multiapproach thermodynamic and kinetic characterization of the thermal hazards of 2,2′-azobis(2-methylpropionate) alone and when mixed with several solvents

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ABSTRACT

Low-temperature azo compounds are a new class of self-reactive materials commonly used as initiators and blowing agents. However, their structure contains a bivalent azo bond, which is quickly released at a high ambient temperature. Self-accelerating decomposition can result in a runaway reaction, fire, or explosion. Therefore, the main issue of this study was to ensure the thermal safety of 2,2′-azobis(2-methylpropionate) (AIBME) by itself and when dissolved in different solvents during manufacturing, storage, or transportation. Adiabatic experiments were performed to investigate the pressure and temperature stress effects on heat accumulation, runaway reaction, and catastrophic conditions. To perform a robust evaluation, both nonisothermal and isothermal conditions were employed to investigate the thermal stability of AIBME against potential hazards. The corresponding kinetic and thermokinetic parameters were obtained using the experimental data and a computational model. Finally, we determined experimentally an apparent activation energy of 109.0 kJ/mol under nonisothermal conditions, which can be used as a reference value for hazard prevention to minimize the cost of accidents caused by uncontrolled temperature conditions.

1. Introduction

A commonly used low-temperature azo compound (azo), 2,2′-Azobis(2-methylpropionate) (AIBME) shares similar characteristics with general azos such as 2,2′-azodi(isobutyronitrile) (AIBN), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA), and 2,2′-azobis-2-methylbutyronitrile (AMBN) in terms of radical generation. It is a noncontained cyano radical and its decomposition products are also nontoxic (Dubikhin et al., 2012; Gowda et al., 2002; Hirano et al., 2005; Li and Koseki, 2005; Yan et al., 2017). For these reasons, AIBME has been widely employed in the synthesis of acrylic materials, adhesives, poly(methyl 2-methylpropenoate), and polyvinyl chloride (Li et al., 2008; Liu et al., 2014; 2015a,b,c). From a kinetic perspective, AIBME is interesting because of its low self-accelerating decomposition temperature (*SADT*), low safe storage temperature, and highly self-reactive properties that can easily trigger reactions (Liu et al., 2014, 2015a,b,c; UN, 2009a,b). However, AIBME is sensitive to external thermal sources and is known to be incompatible with numerous materials, such as acids and bases.

AIBME thus belongs to the 4.1 class in the United Nations recommendations on the transport of dangerous goods and is defined as a pyrophoric material that is intrinsically unstable and reactive (UN, 2009a,b). In China, numerous accidents involving azos have occurred during manufacturing and storage (Guo et al., 2013; Liu et al., 2015a,b,c; Partington and Waldram, 2002; Talat and Bywate, 1954; Zhang et al., 2015). For instance, in 2008, a thermal explosion and runaway reaction involving AIBN occurred in a petrochemical plant and was due to the self-heating of AIBN during its storage or transportation, causing a serious fire and explosion that killed 21 people and injured 59 more (Fig. 1a). In September 2009, a violent chemical accident occurred on a truck loaded with xylene and AIBN in Shandong, China, killing 18 people and injuring 11 others (Fig. 1b). In April 2011, a catastrophic explosion and fire was started during an uncontrolled polymerization of azobis dimethylvaleronitrile (ABVN) (Fig. 1c); on this

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Fig. 1. Thermal runaway reaction and explosion accidents of azo compounds in China. (a) Industry plant, (b) Bus, and (c) Reactor (Guo et al., 2013; Liu et al., 2015a,b,c; Partington and Waldram, 2002; Zhang et al., 2015).

occasion, the entire plant was destroyed, 42 employees were killed, and the fire spread to residential units in the neighborhood. Table 1 lists several selected serious disasters that resulted from the intrinsic hazards of azos. High temperatures or the proximity of thermal sources during manufacturing with, storage of, or transportation of AIBME inevitably induces its thermal decomposition and may trigger a runaway reaction (Deng et al., 2017; Dou et al., 2014, 2017).

The thermal hazards and incompatibility of AIBME were evaluated using differential scanning calorimetry (DSC), a thermal activity monitor III (TAM III), and vent sizing package 2 (VSP2) to characterize its inherent behavior in the presence of an acid or alkaline solution. To compare various upset scenarios, thermokinetic parameters—such as the exothermic onset temperature (T_0), heat of decomposition (ΔH), highest heat flow at time t (W_p), self-heating rate (dT/dt), pressure rise rate (dP/dt) (Wang et al., 2014), and time to maximum rate under adiabatic conditions (TMR_{ad})—were assessed to verify the severity of incompatible hazards in the process. The corresponding kinetic and thermodynamic parameters were determined for the experimental data and the apparent activation energy (E_a) was calculated using well-known equations. We employed DSC test data and advanced kinetics and technology solutions to extract thermokinetic parameters by the differential isoconversional approach (Chen and Shu, 2016).

Considering these important parameters will ensure safer storage or transportation conditions by carefully assessing the thermal hazards of the self-reactive substance of interest. Moreover, to fully appraise the level of the hazard associated with the use of AIBME, the incompatibility of AIBME with an acid or alkaline solution was assessed and a risk matrix for adiabatic runaway reactions was obtained (Ng, 1975; Ni et al., 2016; Sun et al., 2004a,b; Sudol et al., 1996). We propose a hybrid method, an experimental setup, and calculated parameters that can be used for conceptual design and chemical process optimization and for evaluating possible hazardous reactions during handling and even decommissioning.

2. Experimental and method

2.1. Samples

AIBME of 98 mass% was purchased from the ACE Chemical Corp (Shanghai, China) and refrigerated at −30.0 °C to prevent its deliquescence and deterioration. Common acidic and alkaline catalysts, namely 6.0 N H_2SO_4 and 6.0 N NaOH, were purchased from a local supplier and used as references for well-known incompatibility with AIBME.

2.2. Nonisothermal tests using DSC

Scanning experiments were performed using a Mettler TA8000 System coupled with a DSC 821^e measuring cell that can withstand pressure of up to approximately 100 bars. STAR^e software was used to acquire and analyze calorimetry curves. DSC measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature using a controlled approach (Liu et al., 2015a,b,c; STAR^e, 2017).

DSC is regarded as a useful instrument for the evaluation of basic thermal hazards and the acquisition of decomposition curves of reactive chemicals. The experimental conditions employed were as follows:

- Material mass: approximately 3.5–4.0 mg;
- Incompatible material mass: approximately 2.0–2.5 mg;
- Experimental temperature range: 30.0–300.0 °C;
- Heating rates: 0.5, 1.0, 2.0, 4.0, and 8.0 °C/min

2.3. Isothermal tests using TAM III

The TAM III thermostat is a liquid-based system that utilizes mineral oil to quickly dissipate heat and minimize the temperature gradient in the system. The TAM III employs patented thermostat technology to precisely control the liquid bath temperature with 0.0001 °C precision over 1 day and can be operated in isothermal, step-isothermal, or temperature-scanning modes. The average temperature fluctuation of