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Comprehensive runaway kinetic analysis and validation of three azo compounds using calorimetric approach and simulation

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

[a] Department of Ammunition Engineering and Explosion Technology, Anhui University of Science and Technology, Anhui, China
[b] Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology (YunTech), Douliou, Taiwan, ROC
[c] Department of Occupational Safety and Health, Jen-Teh Junior College of Medicine, Nursing and Management, Miaoli, Taiwan, ROC
[d] Department of Safety, Health, and Environmental Engineering, YunTech, Douliou, Taiwan, ROC

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ABSTRACT

To investigate thermal runaway behaviors of three azo compounds (2,2'-azobis isobutyronitrile, 2,2'-azobisisobutyramidine hydrochloride, and 2,2'-azobis-2-methylbutyronitrile), this study focused on a green approach in adopting the usage of resources, reducing pollution, and protecting the environment. Azo compounds are widely used as dyes, pigments, blowing agents, and initiators. We analyzed the thermal hazards and incompatibilities of azo compounds using differential scanning calorimetry and thermal activity monitor III under dynamic and isothermal scanning tests. This study devised an effective method for predicting thermal hazards, runaway conditions, and thermal properties for a reactor containing azo compounds of interest. The thermokinetic parameters were then simulated in a hierarchical group of kinetic reaction models by adopting the advanced kinetics and technology solutions approach. The apparent activation energies were compared with that reported the literature. These results are highly relevant because they represent important parameters for a safer process design and feasible optimization.

1. Introduction

Azo compounds have a rich history of usage in applications involving medicine, paint, rubber, and foodstuffs since their discovery in the twentieth century (Li et al., 2008; Thiele, 2006). These compounds typically have bivalent nitrogen composition that can be readily ruptured to lose nitrogen molecule thermally. Notably, a typical azo compound is attached with functional groups such as R–N=N–R′, where R and R' are either aryl or alkyl groups. Therefore, azo compounds can be used in numerous acid–base catalyzed chemical reactions involving the formation of free radicals, and lead to the formation of by-products in daily life. Therefore, hazard estimation thus involves an area where chemistry and engineering are frequently combined to prevent undesirable incidents (Deng et al., 2017; Dou et al., 2014, 2017; Ni et al., 2016).

Because of the potential risk of self-decomposition during production, handling, transportation, and storage, azo compounds are identified as Class IV in the United Nations classification (Li and Koseki, 2005). The breaking of around the double bond leads to a sudden rise in temperature and pressure, which is responsible for initiating a runaway reaction followed by explosions (Ng, 1975). AIBN (2,2'-azobisisobutyronitrile), a commercially crucial alkyl azo compound, is used as an initiator in polymerization. It can release nitrogen to the atmosphere when heated beyond 100.0–107.0 °C (Liu et al., 2014). Previous studies have revealed that AIBN slowly breaks down at room temperature (Van Hook and Tobilsky, 1958). Therefore, it should be ideally stored below 10.0 °C, and any external heating source should be avoided. AIBA (2,2'-azobisisobutyramidine hydrochloride) is a water soluble, commercially available, and bicationic azo compound that can be used as a surface-attached free radical initiator (Van Hook and Tobilsky, 1958). AMBN (2,2'-azobis-2-methylbutyronitrile), a typical azo initiator, is used to obtain a high polymerization rate in various seeded experiments. Previous studies regarding heat accumulation and storage tests have indicated that AMBN undergoes self-accelerating decomposition when the solid–liquid phase of the sample appears and its melting point lessens (Ramos et al., 2003). Nevertheless, the possibility of a violent runaway reaction cannot be excluded during the manufacturing process, which starts by

* Corresponding author. Department of Ammunition Engineering and Explosion Technology, Anhui University of Science and Technology, Anhui, China.
E-mail address: shucm@yuntech.edu.tw (C.-M. Shu).

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dosing an acid or alkali catalyst for the thermal reaction. Numerous runaway incidents have been reported involving azo compounds because of incorrect kinetic estimation, a lack of thermal hazard awareness, and personal errors, to name a few (Schmid et al., 2006).

In this study, we determined the thermal runaway reaction of three azo compounds, AMBN, AIBA, and AIBN, each alone and mixed with an acid or alkali. Differential scanning calorimetry (DSC) was used to determine thermokinetic parameters, such as apparent exothermic onset temperature (T_0), peak temperature (T_p), and enthalpy (ΔH_d). Thermal activity monitor III (TAM III) was used to determine decomposition characteristics during storage or transportation under isothermal conditions and evaluate incompatibilities, such as highest heat flow, reaction time, and time to maximum rate under isothermal conditions (TMR_{iso}). Thermal imaging camera (TIC) with robust computational algorithms can be used to monitor and grasp runaway reactions which occurs in the liquid or gas phase of the sample; in addition, a solid, liquid, or solid–liquid interface can sufficiently induce a reaction for a lower heating rate.

A green kinetic approach accompanied using DSC at five heating rates of 0.5, 1.0, 2.0, 4.0 and 8.0 °C/min was used to receive thermokinetic parameters for process safety analysis and assessment. This approach involves DSC test data and advanced kinetics and technology solutions to extract the thermokinetic parameters using the isoconversional approach. The results were, in turn, used to evaluate the self-accelerating decomposition temperature (*SADT*) for a package. These approaches can be used for conceptual design and chemical process optimization, and assessing hazardous reaction, safer storage, transportation, handling, as well as even decommission.

2. Experimental and method

2.1. Samples

Ninety-eight mass percent of AMBN, AIBA, and AIBN were procured from ACE Chemical Corporation, Taiwan and stored under dry conditions to prevent them from moisture and their degradation.

2.2. Acid and alkali catalyst

Common acid and alkali catalysts were purchased from a local vendor, and 6.0 N H_2SO_4 and 6.0 N NaOH were prepared for use.

2.3. Differential scanning calorimetry (DSC)

In DSC, according to the change in material energy technology, the enthalpy change of a sample is analyzed. We introduced the sample and reference material in different experimental containers; however, they were placed in the same heating furnace and heated at a constant rate. The azo compounds were sealed in a test crucible that withstands a pressure of up to 100.0 bar. AMBN and AIBA were thermally scanned using the Mettler TA 8000 system DSC 821^e apparatus, and thermal analysis software STAR^e was used to monitor the thermal reaction curve (STAR^e, 2017). The temperature range was 30.0–300.0 °C, and the heating rates applied for the temperature-programmed ramp were 0.5, 1.0, 2.0, 4.0, and 8.0 °C/min. Approximately 5.0 mg of test samples of AMBN, AIBA, and AIBN were used for acquiring the experimental data.

2.4. Thermal activity monitor III (TAM III)

Here, a 25.0 L oil tank creates an environment at a constant temperature. There are two measuring cups for sample and reference in the cylinder. Every measuring cup entails using Peltier thermopile thermal sensors to measure the thermal power released by the sample or reference products. The sample and reference with Peltier detectors were connected in series. The signal principle was based on the sum of the voltage signal from the paired detectors. TAM III and its accessories were fabricated using the thermometric-developed thermostat scanning monitor, and the temperature operating range was 15.0–150.0 °C. The level of sensitivity can reach 10.0 nW, and its temperature error is ±0.01 °C (Product Information, 2017).

TAM III, which was used to evaluate a runaway reaction in the thermal analysis region. The DSC results revealed that the experimental temperatures were lower than T_0 of the samples. Therefore, we can determine maximum heat flow (Q_{max}), ΔH_{iso}, and TMR_{iso} by TAM III.

2.5. Thermal imaging camera (TIC)

In practice, a TIC is a type of thermal graphic camera used in academic institutes and industrial sectors. This type of imaging camera emits infrared radiation and permit researchers to observe heat areas through smoke, darkness, or heat-permeable barriers. TICs are typically handheld or helmet mounted. The TIC employed in this study can record a maximum of 60 frames/s, which allowed users to probe the critical stages of the reaction within the first 300.0 s. A TIC with robust computational algorithms can be used to monitor and grasp runaway reactions and generate information that can be used to forestall future thermal accidents in high-risk operations, such as the storage, transportation, or manufacturing of reactive compounds.

2.6. Reaction kinetic model simulations using advanced kinetics and technology solutions

Kinetic model simulation was employed to determine the thermal safety parameters for chemical reactions of AMBN. The applied green approach has been proven to be an effective technology for using hazardous azo compounds; moreover, it can avoid violent runaway reactions during manufacturing, operation, transportation, storage, disposal, and decommission (Ramos et al., 2003; Sudol et al., 1996). Isoconversional approach provides both model-fit and model-free kinetic analysis (Ozawa–Flynn–Wall and the American Society for Testing and Materials (ASTM)) of a solid-state reaction under non-isothermal and isothermal conditions (Gowda et al., 2002). It determines the Arrhenius parameters, the contribution of different parameters from an applied kinetic model. The investigated reaction at various heating rates (non-isothermal) or temperatures (isothermal) can be simulated after the determination of thermokinetic parameters (Liu et al., 2015).

3. Results and discussion

3.1. Sample analysis using DSC

Azo compounds, here AMBN, AIBA, and AIBN, are thermally unstable, reactive, and heat sensitive because of the presence of bivalent –N=N– bond. The bonds are cleavaged upon heating, and this causes a thermal decomposition reaction.

According to the heat scanning data of AMBN, two endothermic peaks were observed (Fig. 1). The first peak can be noticed at 50.1 °C, which results from the phase change in the AMBN crystal. On increasing the temperature to 51.4 °C, the second peak accompanied by physical transformation was obtained. A preliminary hazard analysis shows that the heat of the reaction of the test sample was 780.9 J/g at 4.0 °C/min, thus classifying the substance as

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