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Assessment of the Thermal Hazard Characteristics of Three Low-Temperature Active Azo Initiators for Polymer Resin in Construction Industries under Adiabatic Conditions

Chia-Feng Tsai* and I-Jyh Wen*

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ABSTRACT: Resins continue to occupy a place in the waterproof building market. Unlike traditional concrete building materials, the polymerization of resins requires initiators to support the required energy to drive the reaction or reduce the polymerization threshold, which shows a high reaction rate and low energy consumption in the polymerization process. Azo compounds (azos) are energetic substances commonly used in polymerization, but they can cause process hazards due to the amount of heat release and accumulation of the resulting heat. To ensure that similar hazards do not occur, the emerging azo initiators 2,2′-azobis(2-methylpropionamide)dihydrochloride (AIBA), 2-cyanopropan-2-yliminourea (CABN), and 2,2′-azodi(2-methylbutyronitrile) (AMBN) are explored. Depending on the process conditions, it is critical to examine how chemical reactions from a laboratory behave at a large scale. Kinetic models can be used to estimate fundamental safety parameters suitable for assessing the reaction hazards and as control measures, such as time to the maximum reaction rate under adiabatic conditions, time to the conversion limit, and runaway determination for process operation. The structure of this study is a combination of adiabatic calorimeter data and a nonlinear adiabatic dynamics model with the goal of helping to fill the void in research on thermal hazard analysis of emerging azo initiators. The adiabatic data is used to analyze the reaction mode characteristics of the azo compounds, and combined with the external environment, the reaction and temperature parameter changes of the azo compounds due to the reaction are discussed in the actual situation.
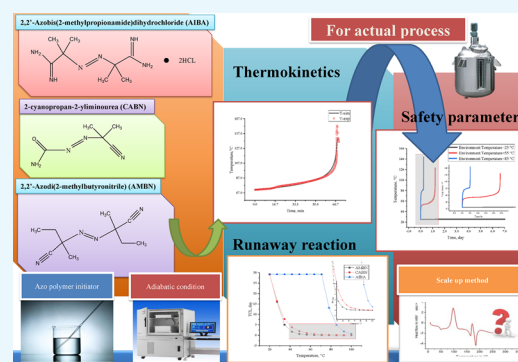
1. INTRODUCTION

Polymer materials are widely used in all walks of life.[1] The reaction in the production process and the properties of the back-end polymers are constructed by raw materials and additives to assist the reaction, such as the reaction initiator promoting the polymerization reaction by its energy production and products from self-reaction. Azo compounds (azos) are a classic initiator with exothermic properties for encouraging the progress of the polymerization reaction due to their thermal decomposition energy and the formation of nitrogen−carbon radicals. This additional energy helps meet the threshold required to catalyze the polymerization reaction, and the reactivity of the free radicals significantly promotes the polymerization of monomers.[2] Due to climate change, polyacrylamide,[3] polyacrylonitrile,[4] and poly(carboxylic acid)[5] have been widely used on the market for waterproof building materials and concrete additives in recent years.[6−8] This trend has spawned more research on azo initiators, driving new species of azos to be used in the field of polymer materials. However, azo initiators have caused thermal hazards in the production and storage processes, causing significant losses to personnel and

property, highlighting the need for thermal hazard assessment of emerging azo initiators.

Reaction hazard characteristics can be obtained based on thermal decomposition disasters.[9−11] For example, on May 12, 2016, a fire broke out in the facilities where azo dye-related materials were placed. After investigation, due to improper temperature control combined with the rising temperature of the environment, part of the azo produces a decomposition reaction and heat release. The exothermic heat further raises the temperature under the lack of heat removal means in the closed environment. The surrounding azo also reacts by increasing the temperature, and a large amount of decomposition heat forms a primary fire source. Inadequate fire control measures make the fire source develop into a fire without control, resulting in this disaster. From the past disasters caused by azos, even the initial

reaction of a small amount of azos due to a slight increase in temperature may still drive the decomposition reaction of other azo substances to cause great losses. Without temperature control procedures, such as poor ventilation, combined with the accumulation of a large number of substances to form heat accumulation, the temperature and time of disasters may be advanced. The means of temperature control can be an essential basis for ensuring the thermal safety of azos. Emerging azos need to be evaluated due to the introduction time, and most of the literature on azo safety lacks a discussion on the thermal hazards of azos in the process mode or adiabatic state. The azo decomposition reaction is closely related to the possible thermal hazards. In addition to safety, the study of the azo reaction mode can also evaluate the process efficiency and energy consumption by analyzing the reactivity, such as the reaction rate and required reaction time. For this purpose, the decomposition character- istics of the azo initiator should be analyzed, and the reaction characteristics and corresponding thermal safety should be estimated based on this analysis. Most of the related literature is concentrated on a single azo, and fewer studies focus on thermal hazard assessment under process conditions. In this study, we selected a well-known water-soluble azo initiator, 2,2′-azobis(2-methylpropionamide)dihydrochloride (AIBA),[12] a newly de-veloped azo initiator with oil/water-soluble properties that can be widely used in various polymerization conditions, 2-cyanopropan-2-yliminourea (CABN),[4] and an azo initiator which has been put into market recognition and application, 2,2′-azodi(2-methylbutyronitrile) (AMBN).[11] The above azo compounds will be analyzed by kinetic and thermal equilibrium calculations to reveal the reaction and thermal hazards..

The kinetic basis of this study comes from accelerating calorimeter (ARC) data. A kinetic model conforming to the experimental data is constructed based on the nonlinear fitting of adiabatic kinetics. The thermal hazard model of the materials under external heat transfer is calculated by combining this model with heat balance. The reaction hazard assessment uses a nonlinear fitting method to make preliminary assessments. In addition, it can further simulate the exothermic behavior of many materials in the process environment to measure the consequences of the cooling system and the runaway reaction.[13]

2. EXPERIMENT PROCESS

2.1. Samples. AIBA, CABN, and AMBN samples were prepared by ACE Chemical Corp., Shanghai, China, and they were all 99.0% by mass with the appearance of white powder solids. The samples were stored at low temperatures before the experiment to keep dry and inhibit self-reactive decomposition.

2.2. Accelerating Rate Calorimeter. The experimental procedure consists of placing a stainless-steel spherical tank with 5.0 g of sample in the furnace into the ARC. The instrument measures the temperature change of the substance in the tank through a thermocouple connected to the tank's surface. At the same time, the instrument system uses the heat−waiting−search (HWS) mode to control the temperature of the tank's outer surface to be consistent with the temperature increase caused by the decomposition reaction of the substance.[14] The temperature change in the tank will be raised to the same level by the tracking heater of the instrument to ensure that the container will not absorb the heat release of the material to achieve thermal data collection under adiabatic conditions. After the sample is heated to a specific temperature, the temperature is kept constant to confirm whether the substance has a self-reactive temperature rise. If not, the heating is repeated and one waits for the next

scanning result.[15] If the self-heating rate is detected to exceed 0.2 °C/min, the temperature and pressure changes are continuously recorded and the current temperature changes are continuously tracked until the overall reaction ends.[15]

2.3. Thermokinetics under Adiabatic Condition. In practice, if a large amount of material produces heat release, it will not be possible to remove the accumulated heat in the container by heat exchange.[16] This kind of system that causes heat accumulation is considered to be in the adiabatic mode. The heat causes the temperature to increase, which also enhances the reaction rate. Rapid generation of heat and gas leads to damage to the process equipment which evolves into a fire and explosion. This phenomenon is characterized by experimental equipment[17] under the assumption that the temperature between the ARC furnace (T_f) and the tank wall (T_w) is equal: $T_f = T_w$, $q_w = 0$ with a phi factor (φ)[18−21]

$$\varphi = 1 + \frac{(c_b m_b)}{(c_s m_s)} \tag{1}$$

The inner tank space of the ARC is approximately 9 cm^3 with a heat capacity of 0.5 J/(g K), and to withstand the pressure difference formed by the reaction, the wall thickness of the tank contributes to the thermal inertia $\varphi = 1.37$. The adiabatic calorimeter ARC's sample and bomb are homogeneous (lumped system). Then, the heat exchange pattern of the ARC system is composed of the energy balance ordinary differential equations and the kinetic equations[22]

$$m_b \frac{d(c_b T_b)}{dt} = (US)_i (T_s - T_b) - W_{loss};$$

$$m_s \frac{d(c_s T_s)}{dt} = W - (US)_i (T_s - T_b);$$

$$W = m_s \frac{dQ}{dt} \tag{2}$$

where c is the specific heat capacity, m is the mass, U and S denote heat transfer coefficient and the surface of heat exchange, dQ/dt is the specific rate of heat generation by the reaction, W_{loss} is the heat loss from the bomb, s and b denote the sample and bomb, respectively, and i denotes the interface between the inner side of the bomb and the sample.

Assuming that (1) the specific heat capacity is constant, (2) the bomb and the sample are in equilibrium i.e., $T_s = T_b$, and (3) the heat loss is negligible, transforming eq 2 yields the following equation

$$(c_s m_s + c_b m_b) \frac{dT_s}{dt} = c_s m_s \varphi \frac{dT_s}{dt} = W; \varphi = 1 + \frac{c_b m_b}{c_s m_s} \tag{3}$$

2.4. Simulation of the Kinetic Behavior. Continuing the above model and expanding it to analyze the description of the adiabatic state kinetic model, the heat exchange can be conveyed as the thermal behavior equation and the corresponding numerical solution analysis between the tank and the furnace body that decompose and generate heat during the solid/liquid reaction.[23]

The basic kinetic background method is composed of the Arrhenius equation and combined with the simplified assumption of the reaction process. The heat model of the container and the sample can be obtained from the heat balance equation[17,24]

Table 1. Parameters of Runaway Characteristics of the Three Azos by ARC

azo compound	mass (g)	T_0 (°C)
AIBA	5.0 ± 0.1	121
CABN		100
AMBN		84

$$W = m_s Q^\infty A f(\alpha) \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

where $R = 8.314$ J/mol/K is the gas constant, A is the pre-exponential factor, E is the activation energy, α is the conversion, and Q^∞ denotes the heat effect of a reaction.

Validated by various research and numerical methods, E_a and A are calculated in relatively well-established models, such as linear regression. $f(\alpha)$[25] is difficult to estimate and present because it covers the overall response pattern[26]

$$A_i \rightarrow \begin{cases} \xrightarrow{r_{i1}} B_{i1} \\ \xrightarrow{r_{i2}} B_{i2} \xrightarrow{r_{i3}} ... \\ ... \\ \xrightarrow{r_{ij}} ... \end{cases} \qquad (5)$$

The reaction mode is characterized by the exothermic mode of the overall reaction[19] with the reaction process (α) and specific reaction rate ($d\alpha/dt$)

$$W = Q_{ij}^\infty \frac{d\alpha_i}{dt}$$

$$\text{where } \frac{d\alpha_i}{dt} = k_{ij} \exp\left(-\frac{E_{ij}}{RT}\right) f_j(\alpha_i) \qquad (6)$$

The reaction model can be divided into single-stage or even multistage reactions.[27] The basic reaction model can be expressed as

$$f(\alpha) = \begin{cases} (1-\alpha)^n & n\text{th model} \\ (1-\alpha)^{n1}(\alpha^{n2}+z) & \text{autocatalysis model} \\ (1-\alpha)(-\ln(1-\alpha))^n & \text{Avrami-Erofeev model} \end{cases} \qquad (7)$$

The kinetic mechanism can be computed by the Thermal Safety software from ChemInform Saint-Petersburg (CISP).[28] The establishment of the reaction mode can further explore the reaction time and rate, which is extremely important in both normal operation and emergency mode, and can be characterized by the time required for the estimated species to reach the maximum reaction rate (TMR_{ad}) and the time required for reaction consumption ($TCLs$). The reaction hazard parameters TMR_{ad} and TCL and temperature change of the azos in the runaway reaction were calculated by kinetics.[16]

2.5. Simulation of Thermal Hazards in a Real Situation. The reaction kinetics can be extended to the thermal equilibrium of systems containing substances, such as vessels, drums, and reactors. For the accumulation of a large number of substances with self-reaction characteristics, the self-decomposition heat from a small part of the substances cannot be released to the outside system, resulting in a temperature increase. If this phenomenon can be diluted by heat conduction on the system's surface, it can be avoided if other unreacted substances in the
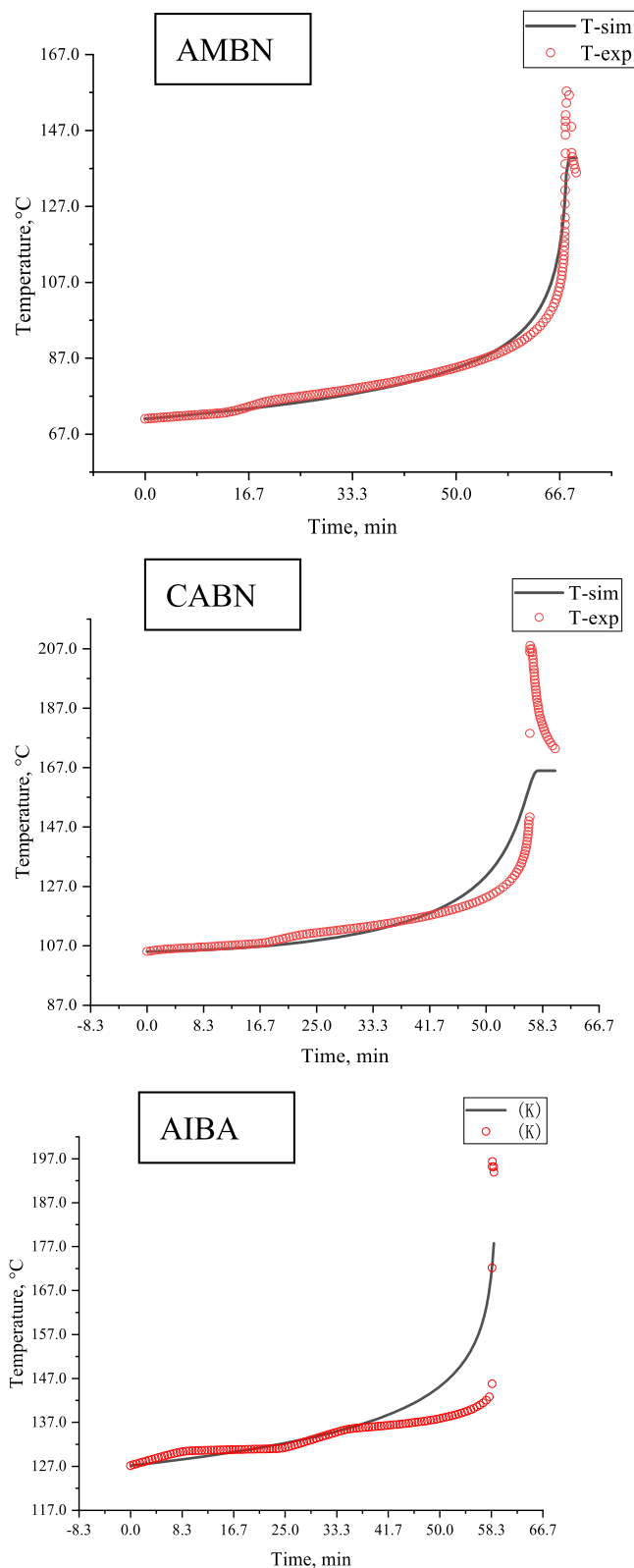
Figure 1. Comparisons of the simulation results of the azos' temperature rise vs time.

system are introduced into the reaction at high temperature; otherwise, many substance reactions are triggered to form runaway reactions. This situation of a rapid temperature increase in a short time must be avoided in hazard control. The basic system heat conduction equation can be expressed as eq 8[29,30]

Table 2. Evaluation Results of the Three Azos under Adiabatic Conditions

	reaction form		$\ln(k_0)$ $(\ln(1/s))$	E_a (kJ/mol)	n1 (dimensionless)	n2 (dimensionless)
AMBN	nth+	first stage	27.2	204.0	1.2	
	nth+	second stage	31.2	118.7	0.5	
	nth	third stage	10.8	144.3	0.8	
CABN	nth+	first stage	53.6	182.2	0.7	
	auto+	second stage	18.7	77.3	1.7	0.3
	auto	third stage	12.2	36.1	1.7	0.6
AIBA	nth+	first stage	35.5	152	0.2	
	auto	second stage	26.0	116.3	1.0	1.2

Table 3. Physical Parameters of AIBA and Packages for AIBA

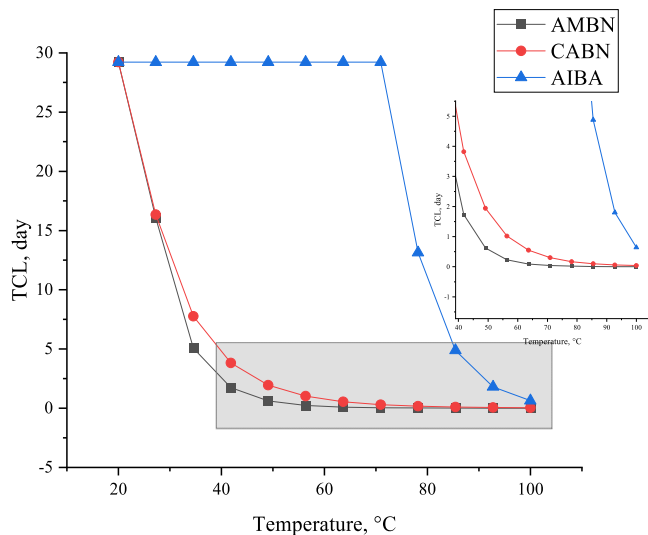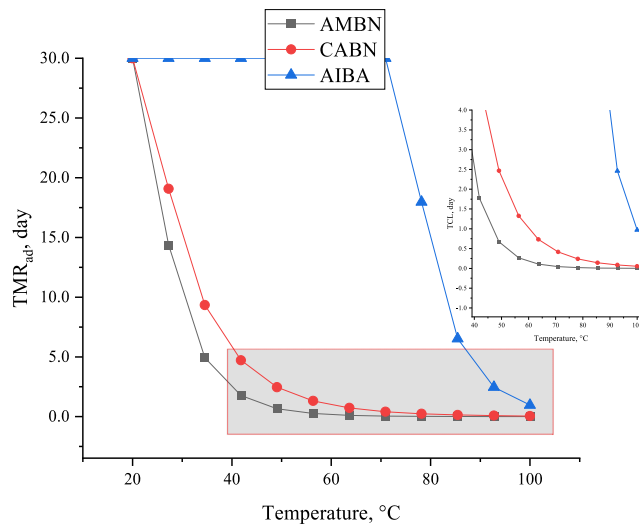| material	size (cm)	shell thickness (mm)	filling height (cm)	density (g/cm)	specific heat capacity (J/(g K))	thermal conductivity coefficient (W/(m K))	heat transfer coefficient (W/(m²·K))
AMBN				0.74	2.0	0.95	10
CABN				0.93	1.5	0.95	10
AIBA				0.91	1.7	0.95	10
25 kg box	$29 \times 39 \times 46^a$	5.0	35	0.75	1.7	0.3	2.2

$^a L \times W \times H.$

Figure 2. Comparisons of TCL at different initial temperatures under adiabatic conditions.

Figure 3. Evaluation of TMR_{ad} at different initial temperatures under adiabatic conditions.

$$\rho C_p \frac{\partial T}{\partial t} = \text{div}(\lambda(\text{grad}(T)) + W) \tag{8}$$

where ρ is the density, C_p is the specific heat capacity, λ is the thermal conductivity coefficient, T is the temperature, and W is the heat generated due to the reaction.

The basic assumption is that the initial temperature inside the system is evenly distributed with the setting of boundary conditions

$$T|_{t=0} = T_i \tag{9}$$

$$\text{first kind}: T_s = T_e \tag{10}$$

$$\text{second kind}: -\lambda \frac{\partial T}{\partial X} \Big|_s = q_e \tag{11}$$

$$\text{third kind}: \lambda \frac{\partial T}{\partial X} \Big|_s = U(T_s - T_e) \tag{12}$$

where X is normal to the surface of the object, subscripts w and e denote the surface and the environment, respectively, and U represents the heat transfer coefficient.

The thermal sensitivity and stability of substances and packaging are related. The evaluation method comes from the self-accelerating temperature during decomposition. However, its test method requires a large number of samples and experimental time. Combining kinetic analysis with heat exchange evaluation model, the corresponding material temperature model can be constructed[19,31−35]

$$\frac{dT}{dt} = \frac{\lambda}{\rho C_p}\left(\frac{\partial^2 T}{\partial m^2} + \frac{g}{r}\frac{\partial T}{\partial m}\right) + -\frac{\Delta H_d}{C_p}\frac{d\alpha}{dt} \tag{13}$$

where C_p is the sample heat capacity, λ is the thermal conductivity, ρ is the density of the azos, x is the package radius, and g is a geometry factor that varies with the type of packaging. ΔH_d and $d\alpha/dt$ are described by adiabatic kinetic models.[30,32,35]

3. RESULTS AND DISCUSSION

3.1. Basic Thermal Parameters Acquisition. Table 1 shows the basic thermal hazard information under the adiabatic H−W−S model test. The temperature tends to rise due to heat accumulation. In the process deviation, the cooling system cannot eliminate the reaction heat, and the temperature exceeds the initial temperature, which accelerates the reaction rate and causes the runaway reaction. The exothermic assessment curve has an inflection point, indicating that the temperature will not return to the initial temperature, and the possibility of a thermal disaster is increased. For example, AMBN will reach a runaway reaction due to the extremely fast reaction rate at $T_0 = 84$ °C. Compared with AIBA and CABN, AMBN has reactive hazard characteristics in a lower temperature range.

3.2. Evaluation of the Thermokinetic Parameters of the Azos. The kinetic simulation is divided into temperature change with signal curves, and the calculated results are shown in Figure. 1, showing that AIBA and AMBN undergo multistage reactions, unlike for CABN. The AIBA and AMBN reaction forms consist of one nth-order reaction with one autocatalysis reactions and three nth-order reactions, respectively. The time required for the reaction showed that AMBN has a larger reaction rate than CABN and AIBA. The reaction rate and apparent activation energy can be used to verify the actual operation and further as the source for estimating the mode of the overall reaction system listed in Table 2, and the material-container-related parameters are shown in Table 3.

3.3. Assessment of the Storage and Transport Hazard Parameters of the Azos. From the change in the *TCL* value in Figure 2, when a lower temperature environment was used, the consumption of AMBN due to the reaction was >70% within 1 day when the temperature was >50 °C. Therefore, firefighting measures are necessary in the actual process operation, whereas additional cooling or rigorous temperature control is less important.

In Figure 3, CABN, AIBA, and AMBN generate the maximum reaction rate at temperatures below 25 °C. The simulation demonstrated that the environmental temperature had a more significant influence on the thermal safety. The runaway reactions of AMBN reach the maximum reaction rate in a short period of time. In actual processes, the use of AMBN requires additional attention to runaway reactions and fire alarms need to be implemented to forestall heat from promoting uncontrolled reactions. AMBN has active decomposition reaction characteristics in a lower temperature environment (>60 °C).

The kinetic expression combined with the numerical simulation of the heat exchange system can evaluate the change of the exothermic behavior when the material is at a specific temperature. Ambient temperature was set at 25 °C, 55 °C, and the onset temperature. The temperature parameter evaluation model can be adopted for thermal hazard analysis of the process reaction, which is used to ensure safe process conditions and establish the safety system design of the process. The results, including the values determined for the runaway situation of the azos, are calculated based on the thermokinetic model. The runaway reaction shows that AMBN has low stability. Figure 4 shows the most appropriate storage conditions for preventing runaway reactions. Great care should be exercised to forestall cooling failure, and it is recommended to refrigerate AMBN for safer storage and transportation.
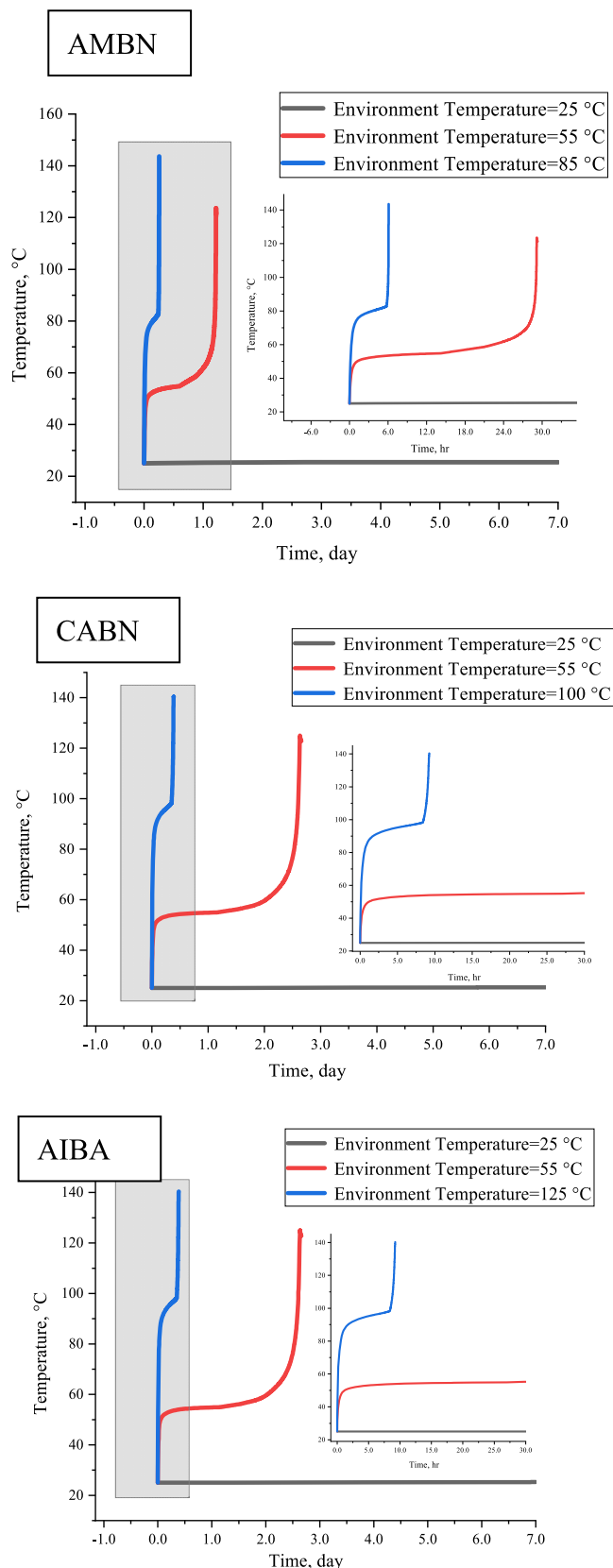
Figure 4. Evaluation of a runaway reaction with a box package under adiabatic conditions with azos.

4. CONCLUSIONS

A nonisothermal ARC experiment is used as the basis of numerical analysis to analyze the exothermic data of azo initiator reactions. The kinetic model curve was calculated by nonlinear fitting and compared with the experimental data of the azo initiator. The mechanical parameters are pushed back to predict the exothermic behavior and related heat transfer of a large amount of material. Simulation analysis was carried out to reduce the tedious and expensive experiments required for hazard analysis. Calculating the reaction behavior of the substances in different external environments in a simulation is helpful to predict the thermal hazards and provide safety measures for practical use.

The TCL and TMR_{ad} showed that AMBN can cause a sudden temperature increase in a short time in the runaway situation, even at low temperatures. From a comparison of the reactive hazard and the subsequent runaway reaction, the hazard of a runaway reaction of azo substances is ranked as follows: AMBN > CABN > AIBA. Therefore, fire protection is a necessary measure and equipment requirement for the application of azo initiators.

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Author Contributions

C.F.T. prepared the manuscript and performed calorimetry and data analysis based on dynamic heat balance conditions and data analysis to evaluate the reaction modes. I.J.W. did the editing and reviewing of the manuscript.

Notes

The authors declare no competing financial interest.

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