

Thermal reactive hazards of 1,1-bis(*tert*-butylperoxy)cyclohexane with nitric acid contaminants by DSC

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Abstract With two active O–O peroxide groups, 1,1-bis(*tert*-butylperoxy)cyclohexane (BTBPC) has a certain degree of thermal instability. It is usually used as an initiator in chemical processes, and therefore reckless operation may result in serious thermal accidents. This study focused on the runaway reactions of BTBPC alone and mixed with various concentrations of nitric acid (1, 2, 4, and 8 N). The essential thermokinetic parameters, such as exothermic onset temperature (T_o), activation energy (E_a), frequency factor (A), time to maximum rate under adiabatic condition (TMR_{ad}) and time to conversion limit (TCL), were evaluated by differential scanning calorimetry at the heating rate of 4 °C min^{-1} , and a kinetics-based curve fitting method was used to assess the thermokinetic parameters. All the results indicated that BTBPC mixed with one more than 4 N nitric acid dramatically increased the degree of thermal hazard in the exothermic peak and became more dangerous. However, it was relatively safe for BTBPC mixed with less than 1 N nitric acid under 34.5 °C.

Keywords 1,1-Bis(*tert*-butylperoxy)cyclohexane (BTBPC) · Curve-fitting method · Differential scanning calorimetry (DSC) · Nitric acid · Thermokinetic parameters

List of symbols

| | |
|-----------------|--|
| A | Frequency factor of reaction ($s^{-1} M^{1-n}$) |
| C_p | Specific heat capacity ($J g^{-1} K^{-1}$) |
| E_a | Activation energy of reaction ($kJ mol^{-1}$) |
| ΔH_d | Heat of decomposition ($kJ kg^{-1}$) |
| k_o | Pre-exponential factor (s^{-1}) |
| m | Mass of reactant (g) |
| N | Normality of nitric acid ($eq mol^{-1}$) |
| n | Order of reaction (dimensionless) |
| n_i | Reaction order of i th stage (dimensionless) |
| Q | Total heat of decomposition ($kJ kg^{-1}$) |
| r_i | Reaction rate of i th stage ($g s^{-1}$) |
| r_{ij} | Reaction rate of i th stage of j th sub-stage ($g s^{-1}$) |
| ΔT_{ad} | Adiabatic temperature rise (°C) |
| TCL | Time to conversion limit (day) |
| T_{max} | Maximum temperature at which the peak point occurs (°C) |
| TMR_{ad} | Time to maximum rate under adiabatic condition (day) |
| T_o | Exothermic onset temperature of reaction (°C) |
| z | Autocatalytic constant (variable) |
| α | Degree of conversion (dimensionless, from 0 to 1) |
| β | Heating rate of DSC experiment (°C min^{-1}) |

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Introduction

Organic peroxides (OPs) are renowned for their thermal instability that lies in the specificity of the oxygen–oxygen

group linkage, which is recognized for its relatively weak bonding dissociation energy (80–200 kJ mol⁻¹) [1]. Accordingly, it is easy to break and form free radical under not very high temperature. Most OPs have one set of symmetrical oxygen–oxygen group, few have two sets.

OPs are widely used in the plastic and rubber industries, often as an initiator to induce free radicals in the initiation of polymerization reaction [2]. In theory, because the RO–OR structure is essentially thermally unstable and easy to form RO• radical, OPs possess many hazardous characteristics, such as thermal sensitivity, large amount of heat evolution upon decomposition, explosion, not to mention their susceptibility to contaminants, inorganic acids (H₂SO₄, HNO₃ or H₃PO₄), alkali solution, and they readily induce radicals under low temperature [3]. Historically, they have caused many fires, explosions, and thermal runaway incidents by heat accumulation, mixed with chemical pollutants, or even mechanical shock worldwide [4–6]. Those situations can occur during manufacturing, storage, transport, or industrial transformation [7]. If the thermal source or contaminants cannot be properly controlled during any stage as previously stated, runaway reactions could be triggered as a consequence and cause an accident [8].

Essentially, 1,1-bis(*tert*-butylperoxy)cyclohexane (BTBPC) is a low volatile, yellowish liquid, symmetrical difunctional (two sets of symmetrical oxygen–oxygen group) peroxide [9], as shown in Fig. 1 [10]. It is used as an initiator of styrene polymerization to give a higher rate of polymerization and a lower residual styrene content. Developed for bulk styrene polymerization it has been discussed elsewhere [11]. BTBPC can initiate polymer growth from two different sites within the same fragment, leading to “double-ended polystyrene,” and then higher molecular weight polystyrene (PS) can be generated at faster rates than applying monofunctional initiators [12]. It is also used as hardener agent for fiber-reinforced PS in the low range temperature.

Even though BTBPC is one of the most commonly used initiators for the commercial production of PS and its copolymers [12], its thermokinetic characteristics are not well understood. Due to the hazardous consequences of decomposition of BTBPC and its extensive use in the

industry, we made efforts to understand the runaway reaction phenomena by evaluating the thermokinetic parameters.

In this study, we measured the basic thermal hazard characteristics of BTBPC, alone and mixed with fixed mass of various concentrations of HNO₃ (1, 2, 4, and 8 N), by thermokinetic evaluation. Since the material is extensively used, there is always the possibility that it could be mixed accidentally, which could occur in normal operation, especially during storage or transport. Process safety parameters must be seriously taken into account for evaluating the degree of hazard based on the thermokinetic parameters. We used differential scanning calorimetry (DSC) to obtain the experimental data sets, which were then used to create useful kinetic models via curve fitting to evaluate the thermal hazard and safety parameters, including exothermic onset temperature (*T*_o), activation energy (*E*_a), frequency factor (*A*), rate constant (*k*), time to maximum rate under adiabatic condition (TMR_{ad}), and time to conversion limit (TCL), etc. [13, 14]. For loss prevention, these safety data are very important information.

In this way, it would be helpful to provide the plants with the necessary information to alleviate the degree of hazard or instruct engineers to design a more effective control system, during runaway excursions in preparation, processing, storage, and transportation.

Experimental and methods

Sample

BTBPC of 70 mass% purity in isoparaffin hydrocarbon solvent, a light yellowish liquid, peroxyketal peroxide, was purchased directly from ACE Chemical Corp., and stored in a refrigerator at 4 °C to keep it stable and away from any external hot condition.

Contaminants

Four types of contaminants were employed for testing the mixing conditions, such as 1, 2, 4, and 8 N HNO₃. The pure nitric acid, obtained from Fluka Corp., was diluted with deionized water to acquire the above-mentioned various concentrations of nitric acid, and then stored in a refrigerator at 4 °C. The quantitative specific contaminant (1.4–2.7 mg) was added into the gold-plated high pressure crucibles and mixed with BTBPC 70 mass% (3.7–5.5 mg). These mixtures with nitric acid were studied to compare the effects of different concentrations of acidity on BTBPC.

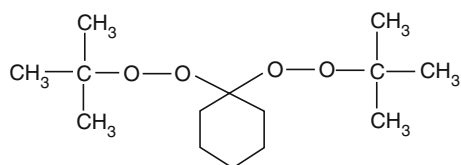


Fig. 1 Structure of BTBPC [10]

DSC

We used a dynamic scanning experiment (Mettler TA 8000 system) and coupled with a DSC 821° measuring test crucible (Mettler ME-00026732), which is high pressure gold-plated steel crucible that can withstand relatively high pressure, ca. 15 MPa [15]. These crucibles are only used for one measurement. A lid is pressed onto the crucible with a pressure of about a ton so that the seal tightens the crucible, and a toggle press is applied to close the crucible. STAR° software was used to acquire thermal curves [15]. The calibrations of temperature and enthalpy for the DSC were performed with indium as a standard. This standard is selected on the basis of their phase transition temperatures (156.6 °C) and enthalpy (28.45 J g⁻¹) situated in the temperature range of interest. The sample mass of the standard was chosen at about 1.0 mg with a heating rate of 4 °C min⁻¹. At the beginning of an experiment, DSC had to be stabilized for 30 min and then the experiments were started with a specific scanning rate for better thermal equilibrium. Here the scanning rate was 4 °C min⁻¹ for each condition of experiments [16]. The range of temperature rise was selected from 30 to 300 °C for each experiment.

DSC is a popular thermoanalytical device that can be employed to detect the temperature change between the sample and reference. From the temperature change between the sample and reference, the heat flow could be detected immediately for viewing on the thermal curves. After the test, the crucible was weighed again, to confirm that there was no leakage during the experiment. This apparatus could properly acquire the heat flow, and then via experimental data we could calculate the T_o , maximum temperature at which the peak point (T_{max}) occurs, and heat of decomposition (ΔH_d) by the interior function of DSC [17]. We used curve fitting to acquire the thermokinetic parameters based on the experimental data of time (s), temperature (°C), and heat power (mW). These data and thermokinetic evaluation were implemented by applying TDPro and ForK software developed by CISP Ltd. [18]. The methods are thoroughly described by Kosoy and Akhmetshin for the creation of a thermokinetic model and the algorithms that are adopted [19]. After these experimental data were fitted, thermokinetic parameters could therefore be obtained.

Safety parameters

Safety is a very serious and important issue. A container system must be maintained safely during the period of process, storage, and transport of the chemicals. The safety parameters must be precisely evaluated for enhancing the safety degree, which could decide whether the cooling

system should be set up or not. Here, we investigated two important safety parameters, TMR_{ad} and TCL. According to the methodologies proposed by Townsend and Tou [20], the results obtained are suitable for the study of the phenomenon of runaway reactions involving pure substance or mixtures. These safety parameters are described below.

Time to maximum rate under adiabatic condition (TMR_{ad})

Time to maximum rate under adiabatic condition is the time instant when a reaction arrives at its maximal rate under adiabatic conditions. Dependency of time to maximum rate on the defined initial temperature of BTBPC is evaluated from the results of series of simulations of a reaction course. TMR_{ad} was proposed by Townsend and Tou [20] who derived two analytical expressions (Eqs. 1 and 2) for calculation:

$$\text{TMR}_{\text{ad}} = \frac{RT^2}{AE_a \Delta T_{\text{ad}}} e^{-E_a/RT} \quad (1)$$

$$\Delta T_{\text{ad}} = \frac{Q}{C_p} \quad (2)$$

The major limitation of this method is that the formulas are valid only for simple single-stage n order reactions. In the case of more complex reactions (including autocatalytic reactions), TMR_{ad} can be properly determined merely by applying a kinetic-based simulation [21, 22]. Accordingly, this method has been employed in the present investigation.

Time to conversion limit (TCL)

Assessment of thermal stability of a substance lies in evaluating the dependency of time instant (TCL) when conversion of a reaction reaches some predefined value—conversion limit (CL), at constant set temperature. Thermal stability is essentially characterized by the time of TCL necessary to reach a certain level of conversion at a specific constant temperature. Therefore, for long-term storage, it can be selected as the maximum permissible time during which the conversion of the product does not have any prominent impact on the product quality. According to the suggestion of Townsend and Tou [20], in this study, we set 10% as the conversion limit value.

Results and discussion

Thermal hazard analysis

All the constituents of the hazardous material and its nitric acid, as contaminant mixtures, are given in

Table 1. The mass ratio (w/w) of BTBPC to HNO₃ was kept about 2:1 to ensure the consistency of results of concentration gradient of nitric acid affected in BTBPC. Table 2 summarizes the thermokinetic parameters that provide reasonable data fitting on each sample, as can be seen in Fig. 2. The parameters were estimated on the basis of two data sets, as delineated in Figs. 3 and 4. By using curve fitting, we could obtain precise thermokinetic parameters.

Figure 2 shows the results of heat flow versus sample temperature of BTBPC alone and mixed with 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹. BTBPC reveals just one smooth single thermal peak. The T_o and peak temperature (T_{max}), as displayed in Table 2, were about 122 and 147 °C, respectively. Table 2 also summarizes the data of the related thermokinetic parameters, such as activation energy (E_a), natural logarithm of frequency factor ($\ln k$),

reaction order (n), heat of decomposition (ΔH_d), and reaction type.

All the thermal curves of exothermic heat flow versus temperature on BTBPC alone and mixed with its contaminant mixtures of 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹ were plotted together as shown in Fig. 2. This figure clearly identifies the differences between these curves. Relevant thermokinetic parameters are also presented in Table 2. The thermal curve of BTBPC + HNO₃ (1 N) is very similar to BTBPC alone. They have almost the same thermokinetic parameters except that BTBPC + HNO₃ (1 N) has higher heat of decomposition. However,

Table 1 Constituents of BTBPC and its HNO₃ contaminant mixtures

| Sample item | Constituents | | | BTBPC/HNO ₃ (w/w) |
|-------------|--------------|------------------------|---------------|------------------------------|
| | BTBPC/mg | HNO ₃ /N/mg | Total mass/mg | |
| 1 | 5.0 | NA | 5.0 | NA |
| 2 | 4.5 | 1/1.4 | 5.9 | 3/1 |
| 3 | 4.5 | 2/2.3 | 6.8 | 2/1 |
| 4 | 5.5 | 4/2.7 | 8.2 | 2/1 |
| 5 | 3.7 | 8/1.8 | 5.5 | 2/1 |

NA not applicable

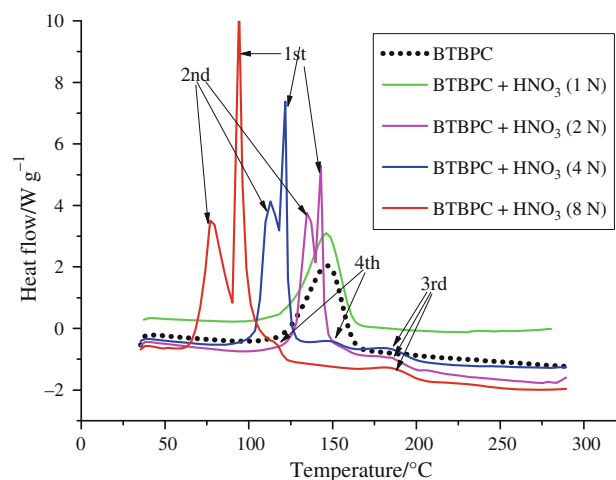


Fig. 2 Thermal curves of heat flow versus temperature on BTBPC and mixed with 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹

Table 2 Thermokinetic parameters derived from the DSC data sets on BTBPC and mixed with 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹

| Sample | Peak number | $T_o/^\circ\text{C}$ | $T_{max}/^\circ\text{C}$ | $E_a/\text{kJ mol}^{-1}$ | n_1 | n_2 | z | $\ln k$ | $\Delta H_d/\text{kJ kg}^{-1}$ | Reaction type |
|--------------------------------|-------------|----------------------|--------------------------|--------------------------|-------|-------|-------|---------|--------------------------------|---------------|
| BTBPC | 1st | 122 | 147 | 157 | 1.08 | NA | NA | 39.89 | 1010 | n Order |
| BTBPC + HNO ₃ (1 N) | 1st | 124 | 147 | 154 | 0.98 | NA | NA | 39.10 | 1118 | n Order |
| BTBPC + HNO ₃ (2 N) | 1st | 121 | 135 | 117 | 1.02 | 1.02 | 0.01 | 31.10 | 620 | Autocatalytic |
| | 2nd | 141 | 143 | 120 | 1.69 | 1.35 | 0.01 | 31.82 | 430 | Autocatalytic |
| | 3rd | 169 | 175 | 120 | 1.14 | 1.04 | 0.01 | 27.82 | 48 | Autocatalytic |
| BTBPC + HNO ₃ (4 N) | 1st | 99 | 113 | 120 | 1.02 | 0.90 | 0.01 | 33.83 | 583 | Autocatalytic |
| | 2nd | 118 | 122 | 120 | 1.16 | 1.08 | 0.01 | 33.83 | 517 | Autocatalytic |
| | 4th | 139 | 147 | 123 | 0.48 | NA | NA | 29.13 | 33 | n Order |
| | 3rd | 169 | 180 | 123 | 0.54 | NA | NA | 26.00 | 62 | n Order |
| BTBPC + HNO ₃ (8 N) | 1st | 65 | 80 | 100 | 1.65 | 0.77 | 0.003 | 30.33 | 917 | Autocatalytic |
| | 2nd | 91 | 94 | 122 | 1.19 | 1.42 | 0.003 | 38.27 | 525 | Autocatalytic |
| | 4th | 110 | 117 | 74 | 1.79 | 0.10 | 0.003 | 19.63 | 614 | Autocatalytic |
| | 3rd | 167 | 183 | 148 | 0.62 | NA | NA | 33.88 | 94 | n Order |

NA not applicable

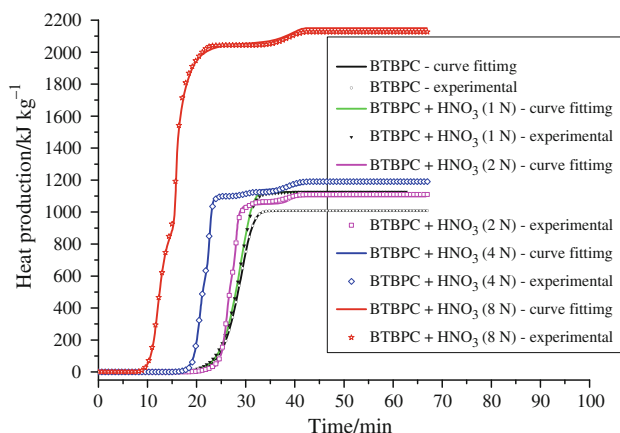


Fig. 3 Heat production versus time with kinetics-based curve-fitting on BTBPC and mixed with 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹

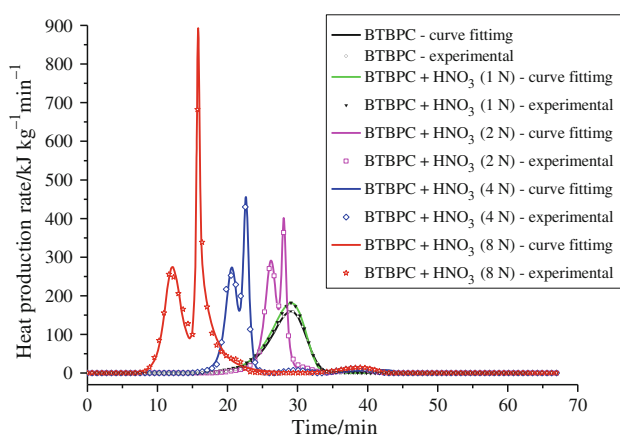


Fig. 4 Heat production rate versus time with kinetics-based curve-fitting on BTBPC and mixed with 1, 2, 4, and 8 N HNO₃ by DSC at 4 °C min⁻¹

the exothermic curve patterns of BTBPC + HNO₃ (2 N), BTBPC + HNO₃ (4 N) and BTBPC + HNO₃ (8 N) is different from those of BTBPC + HNO₃ (1 N) and BTBPC alone. BTBPC mixed with 2, 4, and 8 N HNO₃ shows the major exothermic peak, which splits into two peaks. The 1st peak has higher heat of reaction, but the 2nd peak has higher maximum peak heat flow. All the peaks from BTBPC mixed with 2, 4, and 8 N HNO₃ are shifted to lower T_0 . That means the T_0 was lower and more dangerous.

In addition, we found BTBPC + HNO₃ (2 N) has a 3rd small peak about at 170 °C. Here, its exothermic heat value was 48.20 kJ kg⁻¹, which revealed its decomposition must be more complicated. The same peak also appeared in BTBPC + HNO₃ (4 N) and BTBPC + HNO₃ (8 N), also ca. at 170 °C. It seems that the 3rd exothermic peak did not

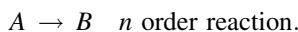
exist at lower concentration of nitric acid mixture, although it existed in higher concentration, whereas independent of concentration of HNO₃.

It is curious that the BTBPC + HNO₃ (4 N) and BTBPC + HNO₃ (8 N) shows a 4th exothermic peak, as shown in Fig. 2. It is closer to the bottom of the 2nd peak. This peak temperature of BTBPC + HNO₃ (4 N) and BTBPC + HNO₃ (8 N) was 143 and 117 °C, respectively, as presented in Table 2. This peak only appeared in higher concentration of nitric acid (4 and 8 N) mixtures, and the higher concentrated nitric acid mixtures, the peak significantly shifted to the lower temperature. It means that BTBPC mixed with higher concentration of HNO₃ (4 and 8 N) is more dangerous than mixed with lower concentration of HNO₃ (1 and 2 N) or BTBPC alone.

Kinetic analysis

STAR^e software coupled with a DSC 821^c can be generally used for kinetic analysis, but it can only calculate an n order reaction. Therefore, we tried to manipulate the simulation function with kinetic models to assess the decomposition of BTBPC and its contaminant, here with HNO₃.

As depicted in Fig. 2, the curve of BTBPC only has a single exothermic peak. The decomposition reaction is expressed below:



The reaction rate (r_i) by this kinetic model is expressed by Eq. 3:

$$r_i = k_0 e^{-E_a/RT} (1 - \alpha)^n \quad (3)$$

where k_0 and E_a denote the pre-exponential factor and activation energy of the n th stage. R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), α is the degree of conversion, from 0 to 1. When BTBPC mixed with 1 N HNO₃ (Fig. 2), the thermal curve, reaction type, and relevant thermokinetic parameters simulated from kinetic model (shown as Figs. 3 and 4) have no difference, so as its decomposition reaction, except that BTBPC + HNO₃ (1 N) has higher heat of exothermic reaction.

For BTBPC + HNO₃ (2 N), not only did the main curve split into two exothermic peaks, but also a 3rd small peak appeared at ca. 170 °C, while the 3rd peak did not appear in BTBPC and BTBPC + HNO₃ (1 N). Therefore, the kinetic model is assumed to be more complicated. The simulated kinetic model of heat production versus time and heat production rate versus time are depicted in Figs. 3 and 4. The decomposition reaction includes two sections, reactions I and II; each reaction type and reaction rate are shown as Eqs. 4–6 as below:

Reaction I



$$\text{1st peak } A \rightarrow B_1 \text{ autocatalytic reaction } r_{i1} = k_0 e^{-E_a/RT} (1 - \alpha)^{n1} (z + \alpha^{n2}) \quad (4)$$

$$\text{2nd peak } B_1 \rightarrow B \text{ autocatalytic reaction } r_{ij} = k_0 e^{-E_a/RT} r_{ij-1}^{n1} (z + \alpha_i^{n2}) \quad (5)$$

Reaction II

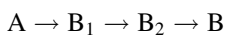


$$\text{3rd peak } E \rightarrow F \text{ autocatalytic reaction } r_i = k_0 e^{-E_a/RT} (1 - \alpha)^{n1} (z + \alpha^{n2}) \quad (6)$$

The kinetic model of BTBPC + HNO₃ (4 N) and BTBPC + HNO₃ (8 N) was more intriguing than the above mixtures. As demonstrated in Fig. 2, the same as BTBPC + HNO₃ (2 N), the curve split into two exothermic peaks, and a 3rd small peak appeared at ca. 170 °C too. Furthermore, there was a 4th peak at these reactions. Accordingly, this kinetic model must be more complicated than the others. The 1st, 2nd, and 3rd reaction types of these two mixtures are all the same: the 1st and 2nd are autocatalytic reactions; the 3rd is *n* order reaction. The reaction type of the 4th peak is different, in that BTBPC + HNO₃ (4 N) was an *n* order reaction, BTBPC + HNO₃ (8 N) was an autocatalytic reaction. Their simulated kinetic model of heat production versus time and heat production rate versus time are also depicted in Figs. 3 and 4. The decomposition reaction also included two sections. Each reaction type and reaction rate is shown in Eqs. 7–12 as follows:

which means that mixing with nitric acid contaminant would promote the reaction being advanced. Furthermore, the total exothermic heat of decomposition (ΔH_d) was also varied. BTBPC + HNO₃ (1 N) and BTBPC + HNO₃ (2 N) had almost the same T_o (ca. 122 °C) and slightly bigger ΔH_d (ca. 1,100 kJ kg⁻¹). The heat of decomposition (ΔH_d , ca. 1,200 kJ kg⁻¹) about more concentration of BTBPC + HNO₃ (4 N) was also slightly bigger than BTBPC + HNO₃ (1 N) and BTBPC + HNO₃ (2 N), but its T_o became lower than BTBPC alone, so it started to reveal the danger of acid contaminant. High concentration of BTBPC + HNO₃ (8 N) was sharply increased ΔH_d to 2,200 kJ kg⁻¹ and considerably decreased its T_o to a lower temperature. The higher the concentrated HNO₃ contaminant mixture was, the greater degree of thermal hazard was.

Reaction I



$$\text{1st peak } A \rightarrow B_1 \text{ Autocatalytic reaction } r_{i1} = k_0 e^{-E_a/RT} (1 - \alpha)^{n1} (z + \alpha^{n2}) \quad (7)$$

$$\text{2nd peak } B_1 \rightarrow B_2 \text{ Autocatalytic reaction } r_{ij} = k_0 e^{-E_a/RT} r_{ij-1}^{n1} (z + \alpha_i^{n2}) \quad (8)$$

$$\text{4th peak (4 N) } B_2 \rightarrow B \text{ } n \text{ order reaction } r_{ij} = k_0 e^{-E_a/RT} r_{ij-1}^n \quad (9)$$

$$\text{4th peak (8 N) } B_2 \rightarrow B \text{ Autocatalytic reaction } r_{ij} = k_0 e^{-E_a/RT} r_{ij-1}^{n1} (z + \alpha_i^{n2}) \quad (10)$$

Reaction II



$$\text{3rd peak } E \rightarrow F \text{ } n \text{ order reaction } r_i = k_0 e^{-E_a/RT} (1 - \alpha)^n \quad (11)$$

$$\text{3rd peak } E \rightarrow F \text{ } n \text{ order reaction } r_i = k_0 e^{-E_a/RT} (1 - \alpha)^n \quad (12)$$

After the nitric acid was mixed with BTBPC, the configuration of the peaks was varied. In this study the 2nd, 3rd, and even 4th peaks were induced. In addition, all of the T_o shifted to lower temperature,

Safety parameters analysis

TMR_{ad} and TCL are important parameters during the process, storage, and transport of energetic materials.

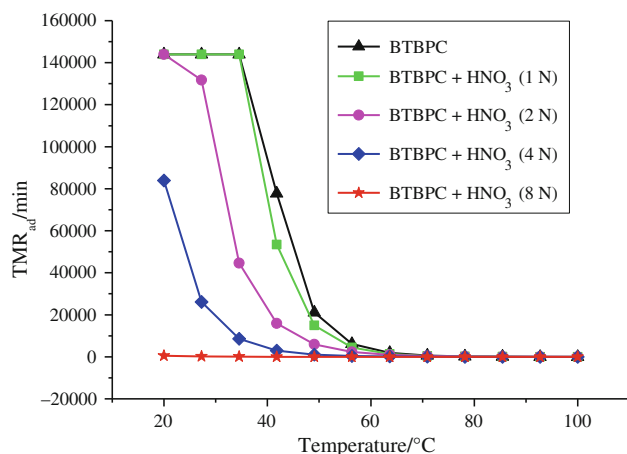


Fig. 5 TMR_{ad} versus temperature curves on BTBPC and mixed with various concentrations of HNO_3

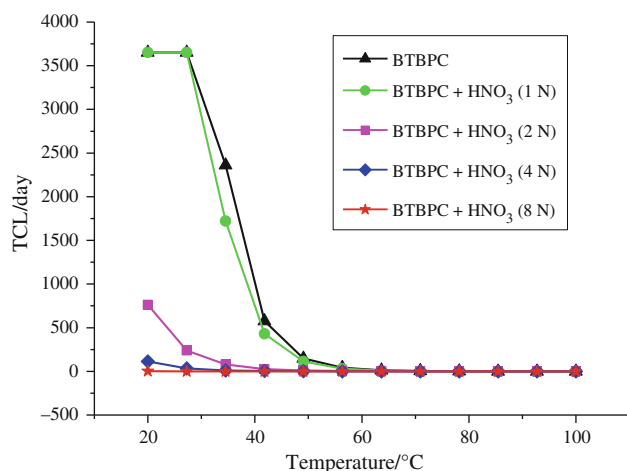


Fig. 6 TCL versus temperature curves on BTBPC and mixed with various concentrations of HNO_3

Further analysis of the hazardous potential of BTBPC and the effect of nitric acid can be accomplished by comparing the values of TMR_{ad} and TCL. Figures 5 and 6 show the dependencies of TMR_{ad} and TCL on temperature calculated on the basis of the kinetic models. TMR_{ad} follows from Fig. 5 that, within the range 20–60 °C, BTBPC + HNO_3 (8 N) is most likely to trigger runaway. It only needs 5.7 min when reaction reaches its maximal rate under adiabatic conditions at 56 °C, while BTBPC + HNO_3 (4 N) needs 412 min. However, for less than 1 N HNO_3 the results revealed relatively insignificant effect on BTBPC.

TCL can be schematized as Fig. 6 as 10% of the conversion limit value. Same as TMR_{ad} , within the range 20–60 °C, BTBPC + HNO_3 (8 N) is likely to induce runaway too. It only requires 7.2 min when a reaction reaches its maximal rate under isothermal conditions at

56 °C, whereas BTBPC + HNO_3 (4 N) requires 353 min. But for less than 1 N HNO_3 , the results revealed relatively insignificant effect on BTBPC.

Conclusions

Runaway reactions by employing the simulations for this study were obtained from the kinetic model of BTBPC alone and mixed with different concentrations of nitric acid as target contaminants.

In this study, we reached the following conclusions:

- (1) BTBPC mixed with less than 1 N nitric acid was safe at temperature below 34.5 °C. More dangerous situations lie on BTBPC + HNO_3 (4 N), especially with 8 N nitric acid.
- (2) The exothermic peak pattern was simple for BTBPC alone and BTBPC with less than 1 N nitric acid. There was just one smooth single thermal peak.
- (3) The exothermic peak pattern of BTBPC + HNO_3 (2 N), BTBPC + HNO_3 (4 N) and BTBPC + HNO_3 (8 N) included a set of split peaks and another one or two small exothermic peaks. The first split peak is wider, and the second split peak is higher. From the effects of nitric acid, all the peaks shifted to the lower T_o , exacerbating the process to a dangerous environment.
- (4) BTBPC alone and BTBPC + HNO_3 (1 N) was an n order reaction. BTBPC + HNO_3 (2 N) has three autocatalytic reaction stages. BTBPC + HNO_3 (4 N) and BTBPC + HNO_3 (8 N) are more complicated with four different reaction stages. The former was autocatalytic, autocatalytic, n order, n order, and the latter was autocatalytic, autocatalytic, n order, autocatalytic reaction, respectively.

A runaway reaction should, by all means, be avoided. Here, more than 4 N HNO_3 should not be allowed to be mixed with BTBPC.

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