

Thermal risk evaluation on decomposition processes for four organic peroxides



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ABSTRACT

Four widely used organic peroxides, namely DTBP, DTAP, BTDH and TBPB, were investigated for hazards caused by their thermal instabilities. Chemically pure materials without diluents were adopted to reveal their thermal decomposition and associated kinetic processes. DSC was employed to carry out experimental thermal study and the Friedman isoconversional method, the Kissinger method, as well as AKTS software were used for kinetic calculations and numerical simulations. Experimental results showed TBPB had the lowest detected “onset temperature”, and unlike DTBP, DTAP and BTDH, all of which showed a two-stage decomposition, TBPB decomposition occurred in a single stage. Heats of reactions measured by ARC were between ca. 37 and 54% of the heats of reaction measured by DSC and reported elsewhere by both, DSC and ARC. The obtained values are compared and discussed. Then, a risk diagram was established to determine the conditionally acceptable conditions of use for the OPs. Furthermore, pressure evaluation results by TS^u indicated the generation of non-condensable gas during runaway reactions should be seriously considered.

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1. Introduction

Organic peroxides (OPs) are widely used in chemical transformations due to the free radicals provided by the peroxy group (–O–O–) in their molecules. Their outstanding properties make them eminently suitable as polymerization initiators, curing agents for unsaturated polyester, cross-linking agents, and other functional materials in industry. However, like a double-edged sword, the relatively weak O–O bond creates thermal instability and potentially explosive properties in OPs. The thermal explosions or runaway reaction incidents involving OPs has been an important safety topic in many countries [1–9]. Accidents involving chemicals and explosions usually have the greatest potential of being fatal [10–15]. According to the CSB database, out of a total of 167 serious incidents that happened in the past two decades in the United States, there were 11 incidents caused by organic peroxides [16]. As a consequence, it is critical to take all available means to prevent unnecessary losses. To explore thermal hazards during OPs' handling, processing and storage, different calorimeters have been employed [17,18]. However, the previous researches were mainly focused on diluted OPs. Although the results obtained can be references for the industrial usage, it is still difficult to understand the

decomposition mechanism and thermal risk of those pure OPs due to the diluents used. At the same time, papers comparing the thermal behavior of different OPs using the same calorimeter and an identical testing method are seldom seen.

In this paper, thermal decomposition processes and risks of four chemically pure OPs (di-tert-butyl peroxide (DTBP), bis (1,1-dimethylpropyl) peroxide (DTAP), 2,5-dimethyl-2,5-di (tert-butylperoxy) hexane (BTDH) and tert-butyl peroxy benzoate (TBPB)) were investigated using both experimental and simulation methods. A standard thermal calorimeter, DSC, was employed to study the thermal behavior of the four OPs, and the results were analyzed based on their similar molecular structures. Combined with experimental results, kinetic calculations and numerical simulations were also conducted to evaluate the thermal risks of the four OPs. To verify the correctness of the experimental data provided by ARC, the results of the heat of reaction measured by DSC and obtained by ARC were compared. Additionally, the simulation results provided by Advanced Kinetics and Technology Solution software (AKTS) were discussed.

Thermal analysis study of OPs is important not only for understanding the kinetics of their thermal decomposition but also for assessing the effect of their exothermic decomposition on the potential hazards [19]. The main hazard is not the thermal decomposition itself but the generation of non-condensable gas (primarily oxygen) that accompanies it. This can lead to a rapidly increasing overpressure in any closed, sealed container that has inadequate

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Table 1
Organic peroxides selected in this study.

| Sample name | Purity | M.F. | CAS no. | Density (g mL ⁻¹) | Supplier |
|---|-----------|--|------------|-------------------------------|--|
| 1 Di-tert-butyl peroxide | DTBP, 98% | C ₈ H ₁₈ O ₂ | 110-05-4 | 0.80 | Sinopharm Chem. Reagent Co., Ltd. |
| 2 Bis-(1,1-dimethylpropyl) peroxide | DTAP, 98% | C ₁₀ H ₂₂ O ₂ | 10508-09-5 | 0.82 | Sinopharm Chem. Reagent Co., Ltd. |
| 3 2,5-Dimethyl-2,5-di (tert-butylperoxy) hexane | BTDH, 92% | C ₁₆ H ₃₄ O ₄ | 78-63-7 | 0.88 | Shanghai Aoke Pharmaceutical Co., Ltd. |
| 4 Tert-butyl peroxybenzoate | TBPB, 98% | C ₁₁ H ₁₄ O ₃ | 614-45-9 | 1.04 | Aladdin Chem. Co., Ltd. |

pressure relief venting. This in turn may lead to vessel rupture and the creation of missiles that can further damage nearby process facilities [20]. DSC does not have the capacity to record the pressure rise that accompanies the decomposition but some other screening or adiabatic calorimetry test methods do not suffer from this limitation. Therefore, the pressure generation trajectories of the four OPs were studied here by means of thermal screening unit, TS^u.

Results in this paper may be used as a reference for further study, thermal risk evaluation, and safety precautions for these four OPs in petroleum and industrial chemical fields.

2. Experimental

2.1. Thermal decomposition tests setup

In this research, the thermal decompositions of four different OPs were studied by means of differential scanning calorimeter, DSC (DSC1, Mettler Toledo), with extra pure nitrogen purging (30 mL min⁻¹). Details of the sample information are listed in Table 1. In order to clarify the effect of heating rate on their thermal behaviors, tests were run under four different heating rates β (1, 2, 4, and 8 K min⁻¹). Stainless steel high-pressure crucibles were employed in tests so as to minimize mass loss during the course of the test. All sample masses were around 3 mg, listed in Table 2. Indium (99.999%) was used to calibrate the energy of the DSC and adjust the instrumental constant to be one. For temperature calibration, indium and zinc were run respectively in low temperature and high temperature sections at heating rates of 1, 2, 4, and 8 K min⁻¹. The reference material was Al₂O₃, and baseline drift was deducted from every DSC curve.

The risk diagram method [21] was used to evaluate the thermal risk for these materials. After calculating the activation energy E based on non-isothermal tests, the adiabatic thermal runaway trajectories for each OP were predicted through simulation. The sensitivity of accelerating rate calorimeter (esARC, THT) used to compare with simulation results is 0.02 °C min⁻¹. Based on the relationships between time to maximum rate under adiabatic condition (TMR_{ad}) and the initial temperature, the conditionally accepted risk areas for OPs are determined.

2.2. Pressure evaluation methodology

The thermal screening unit (TS^u) is a piece of equipment that allows screening substances safely for thermal runaway [22]. On performing a test the user controls the ramp rates of the oven. After an initial delay due to “thermal lagging” effect, the sample temperature will be found to follow the oven ramp at the same

Table 2
Sample mass for each DSC test.

| Heating rate (K min ⁻¹) | Sample mass (mg) | | | |
|-------------------------------------|------------------|------|------|------|
| | DTBP | DTAP | BTDH | TBPB |
| 1 | 3.02 | 2.94 | 3.00 | 3.09 |
| 2 | 2.94 | 3.06 | 3.04 | 3.07 |
| 4 | 2.96 | 3.06 | 3.00 | 3.05 |
| 8 | 2.96 | 3.05 | 3.04 | 3.03 |

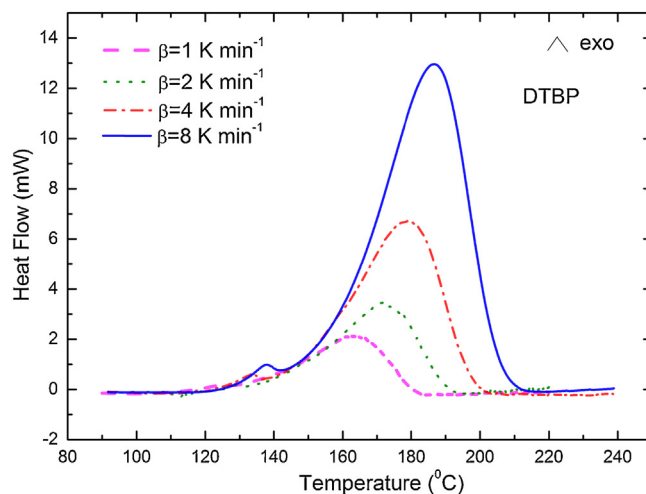


Fig. 1. Heat flow curves for DTBP under 4 heating rates.

rate with a slight offset. In addition to temperature data, the TS^u is also equipped with a pressure transducer that records changes in sample pressure as the reaction proceeds.

Experiments were performed with 316ss construction test cells around 8 mL in volume. The temperature was ramped in 1 K min⁻¹ from room temperature after sample charging.

3. Results and discussion

3.1. Thermal decomposition of samples

The decomposition of organic peroxide is a complex process starting with the break of the O–O bond [23]. Figs. 1–4 illustrate the heat flow curves versus temperature for the decomposition of the four samples at heating rates β (1, 2, 4, and 8 K min⁻¹). Each sample shows one major exothermic peak without endothermic valleys. The major exothermic peaks of DTBP and DTAP are preceded by

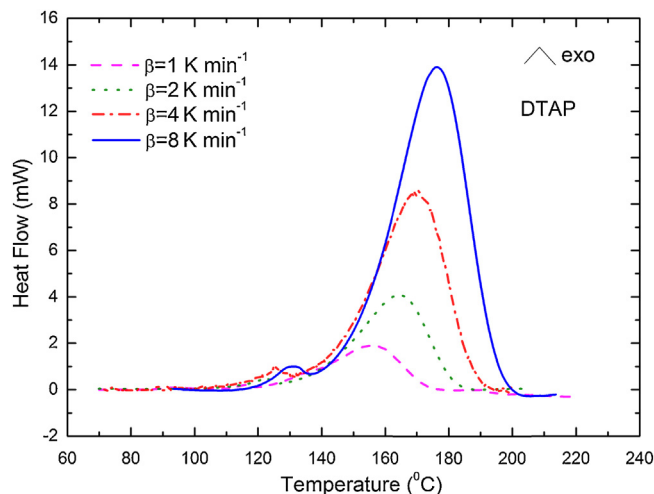


Fig. 2. Heat flow curves for DTAP under 4 heating rates.

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