

THERMAL RUNAWAY HAZARDS OF *tert*-BUTYL HYDROPEROXIDE BY CALORIMETRIC STUDIES

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Thermal runaway reactions associated with exothermic behaviors of *tert*-butyl hydroperoxide (TBHP) solutions and TBHP reacting with alkaline contaminants were studied. A differential scanning calorimetry (DSC) was used to characterize these inherent behaviors of TBHP solutions with KOH, NaOH, LiOH and NH₄OH. The exothermic peak in thermal curves of TBHP solutions with different alkali were detected by DSC thermal analysis. By thermal analysis, we compared various heats of decomposition of TBHP solutions with alkaline impurities, and determined the incompatible hazards of various TBHP solutions with alkaline contaminants. Comparing with TBHP in various diluents, the adiabatic runaway reaction via vent sizing package 2 (VSP2) indicated that aqueous TBHP intrinsically possesses the phenomena of thermal explosion with dramatic self-reactive rate and pressure rise under adiabatic conditions. Many commercial organic peroxides may have different hazard behaviors. Therefore, using thermal method to classify the hazards is an important subject.

Keywords: alkaline, differential scanning calorimetry (DSC), runaway reactions, *tert*-butyl hydroperoxide (TBHP), vent sizing package 2 (VSP2)

Introduction

The thermal decomposition of hydroperoxides proceeds partially by molecular homolysis due to the peroxy group (–O–O–) which leads to a tendency for spontaneous decomposition to more stable products. *Tert*-butyl hydroperoxide (TBHP) is a typical alkyl hydroperoxide for commercial and industrial applications. It can be characterized by the presence of the hydroperoxy group in the molecule, which is intrinsically unstable or labile to radical-induced, ionic-induced, thermal or incompatible decomposition. Hydroperoxides, such as hydrogen peroxide, cumene hydroperoxide (CHP) and *tert*-butyl hydroperoxide are extremely sensitive and incompatible to acids, base, metal ions, and other impurity. It is one of the initiators for emulsion and suspension polymerization of ethylene, vinyl acetate, acrylates, polyvinyl chloride (PVC), or curing agent for unsaturated polyesters in the petrochemical industries. The main application of TBHP is as a source of tertiary-butyl derivatives including esters and alkyl peroxides. Commercially, TBHP solution in water and in most hydrocarbon solvents is widely prepared and in prevailing use.

Organic peroxides vary in thermal hazards from self-reactive decomposition to the potential for the fire

or explosion accidents, not to mention their environmental impact. A great number of formulations with a wide range of safety-related properties, manufacturers or users involve hazard identification and classification problems. The National Fire Protection Association (NFPA) has suggested five classes (Classes I–V) of organic peroxides to provide the compatible diluents and maximum storage amounts with various organic peroxides. The classified description of TBHP given by NFPA 432, Code for the Storage of Organic Peroxide Formulations, is either as Class I (deflagration), Class II (severely reactivity and fire hazard), or Class IV (ordinary combustible) formulations in various concentrations and diluents which are water and *tert*-butanol, di-tertiary butyl peroxide and *tert*-butanol, and water, respectively. The maximum individual container sizes are 5 or 55 gal with different concentrations, classes and transport containers [1].

According to the NFPA recommendation, TBHP is readily capable of explosive decomposition or runaway reaction even at normal temperature and pressure (NFPA 704). The commercial formulation of TBHP 70 mass% diluted with water requires elevated temperatures and pressures for decomposition to occur, and is considered to combust in the same manner as ordinary combustion (NFPA 432). However, the Department of Transportation (US DOT) has not yet set the recom-

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mended maximum temperature for control or emergence. As for safe handling procedures, transportation and storage, a better understanding of the basic properties of organic peroxides is required. Misinformation or inadequacy in handling organic peroxides, particularly as applied to safety, should be prudently taken into account.

To identify the hazards of organic peroxides, the United Nations (UN) Committee of Experts on the Transport of Dangerous Goods (TDG) has classified TBHP as Organic Peroxide Type F that is allowed for transport in tank containers in specific commercial packages; the suggested storage temperature should be controlled at less than 30°C during transportation. The TDG has also suggested that the concentration of TBHP solution suitable for transport in tank-containers should not be more than 72 mass% with water [2]. AIChE's Design Institute for Emergency Relief System (DIERS) program proposed vent sizing methodology for TBHP in the case of emergency relief. For a runaway reaction, the vent area suggested was 0.0014 m² per 1000 kg TBHP (10 mass%) at relief set of 689.5 kPa and 172°C under tempered/vapor flow system [3].

An explosion caused by a tank of TBHP injured 19 people due to a cooling failure in Taiwan [4]. For some runaway incidents caused by hydroperoxide or ketone peroxide, the temperatures of reaction, during transportation, or storage were even as low as ambient temperature. However, few reviews or previous studies with hydroperoxides have been conclusive as to whether significant reactivity hazards even exist. The thermal decomposition and self-reactive properties of these unstable organic peroxides require to be clearly identified, and more efforts are needed for reactive, self-reactive or incompatible studies. The aim of this research was to verify thermokinetic data, such as heat of decomposition (ΔH), exothermic onset temperature (T_0), of TBHP solution with alkaline contaminants by using DSC calorimetry. By comparing the different incompatible behaviors of TBHP in different alkaline diluents, a new insight of reactive or self-reactive hazards of TBHP might be suggested for an alternative way to process, storage and transportation.

Experimental

Materials

Tert-butyl hydroperoxide (TBHP) solutions of 70 mass% in water were purchased from Merck Co., then stored in a refrigerator at 4°C; and NaCl, KOH, NaOH, LiOH, and NH₄OH were directly acquired from Mallinckrodt Baker Inc.

DSC

Dynamic temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821^e apparatus with high pressure gold-plated crucible (ME-26732) which was sealed manually by a special tool equipped with Mettler's DSC and could withstand high pressure until 15 MPa. STAR^e software was used to obtain thermal curves and to analyze the chemical kinetics. Heating rate chosen for the temperature-programmed ramp was at 4°C per minute from 30 to 300°C to maintain better thermal equilibrium [5].

VSP2 (vent sizing package 2)

Vent sizing package 2, manufactured by Fauske & Associates, Inc., is a PC-controlled adiabatic calorimetry with a pressure and temperature system that balances the internal and external pressure and temperature of the system. An adiabatic calorimeter with low heat capacity of the test cell essentially ensures that all the reaction heat released remains within the tested sample. The very thin-walled sample container of the VSP2 has an inside volume of about 100 mL and the thermal inertia factor (ψ) of the test cells is from about 1.05 to 1.20 that can be used to assess the thermal data and then be directly extrapolated to the process conditions. For a reactive system, overpressure in a vessel is normally due to heat of decomposition that obeys the overall energy balance of the reactants and products. Both pressure and temperature equalization techniques are used. The former enables the test cell to maintain its integrity at elevated pressures and the latter enables the temperature of sample cell and outer guard container to remain equal by the usual adiabatic temperature. The pressure is built up in the closed test cell, then it will be automatically compensated for by pressure of equal magnitude in the enclosing pressure vessel. To assure the normal operation of this apparatus and avoid bursting the test cell, TBHP 15 mass% was deliberately selected concentration for the VSP2 experiments. The injected volume of TBHP 15 mass% was mandated at 50 g into a stainless steel 316 cylindrical test cell with inside volume of about 100 mL and net mass of 26 g. A standard heat-wait-search procedure was followed to conduct the adiabatic runaway test. If there was any significant temperature or pressure increase with respect to time, then the program terminated the HWS step, switched off the main heater and turned on the guard heater for closely tracking any runaway reaction.

Table 1 Heats of decomposition and initially exothermic temperatures of TBHP solutions with various alkaline contaminants by DSC trials

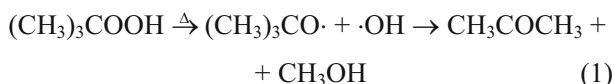
Sample	Alkaline	Mass ^b /mg	Initially exothermic temp., $T_{on}/^{\circ}\text{C}$	Heat of decomp. $\Delta H/J\text{ g}^{-1}$	Peak temp./ $^{\circ}\text{C}$
TBHP ^a	–	4.40	75.0	1622.4	161.8/234.6
	NaOH	9.07	40.0	1491.3	181.2
	KOH	8.09	40.0	749.5	98.9
	LiOH	8.44	40.0	1122.2	178.1
	NH ₄ OH	11.87	60.0	1286.6	152.9
	NaCl	9.54	40.0	1609.1	184.9

Here, ^aTBHP 70 mass% in water (H₂O), 100 mass% TBHP in water solution in this experiment, ^bTBHP:alkaline=10:1

Results and discussion

Thermal decomposition of TBHP

Hydroperoxide is well known to follow a rapid exothermic decomposition reaction with a complex mechanism and initiator/catalyst. In particular, the spontaneous decomposition of free-radical compounds releases heat, which causes a rise in temperature. The photolytic or thermal decomposition of TBHP either neat (liquid phase) or in inert solvents (carbon tetrachloride and chlorobenzene) occurs with liberation of oxygen and formation of *t*-butyl alcohol. In the gas phase, however, acetone and methanol are produced from the breakdown of the *tert*-butoxy radicals with less oxygen being evolved. In practice, a hypothetical but energetically reasonable decomposition reaction has been proposed as follows [6]:



For TBHP in a reactive solvent, the initially formed radicals will interact with a specific solvent by either abstracting hydrogen or by addition to olefinic binds. Such alkyl radicals generated from the solvent can induce the decomposition of the hydroperoxide, apparently more effectively than the initially formed alkoxy radicals [7–9]. Thermal hazards of TBHP are essentially related to concentration contaminants and diluents. For thermal analysis, non-isothermal calorimetry was executed to measure the behaviors and characteristics of the exothermic decomposition of TBHP solution with alkaline by using a programmed scanning test.

Thermal analysis on DSC non-isothermal method

The initially exothermic temperature and heat of decomposition of TBHP 70 mass% in water with various alkaline contaminants were simply acquired by using DSC with quantitative tests. Figures 1–6

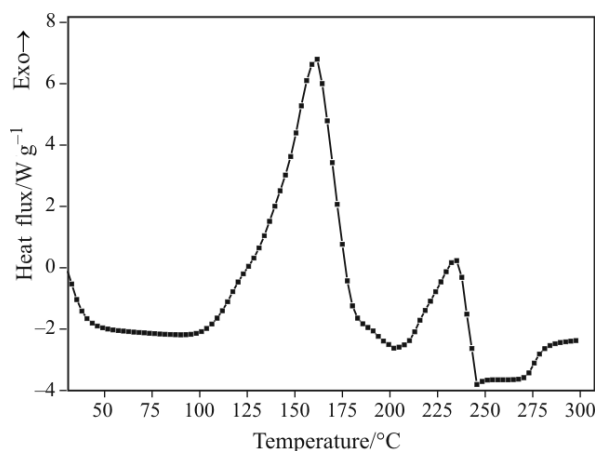


Fig. 1 Thermal curves of TBHP 70 mass% solutions by DSC trials

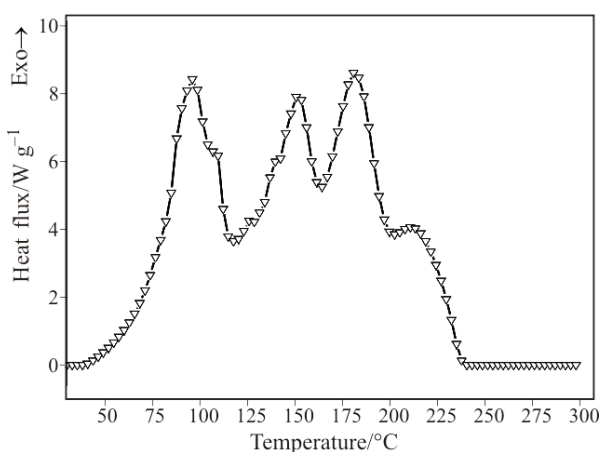


Fig. 2 Thermal curves of TBHP solutions with 6 N NaOH_(aq) by DSC trials

depict the typical thermal curves vs. temperature for the exothermic decomposition of TBHP/NaOH, TBHP/KOH, TBHP/LiOH, TBHP/NH₄OH and TBHP/NaCl solutions. NaCl was used to distinguish the ion-induced effect. By comparison, the thermal curves illustrate the differential exothermic pheno-

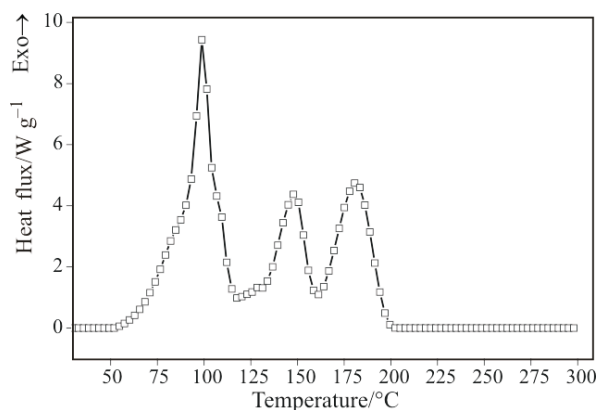


Fig. 3 Thermal curves of TBHP solutions with 6 N KOH_(aq) by DSC trials

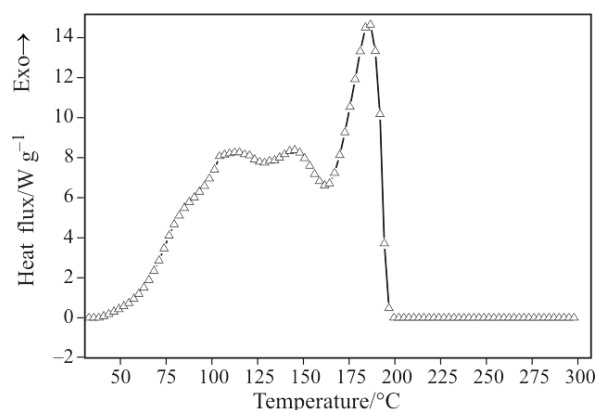


Fig. 6 Thermal curves of TBHP solutions with saturated NaCl_(aq) by DSC trials

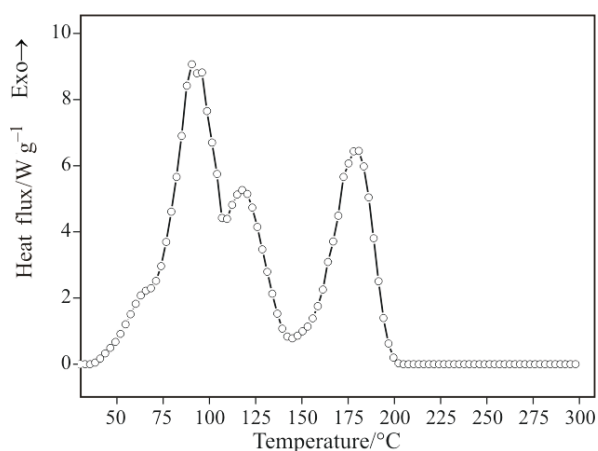


Fig. 4 Thermal curves of TBHP solutions with saturated LiOH_(aq) by DSC trials

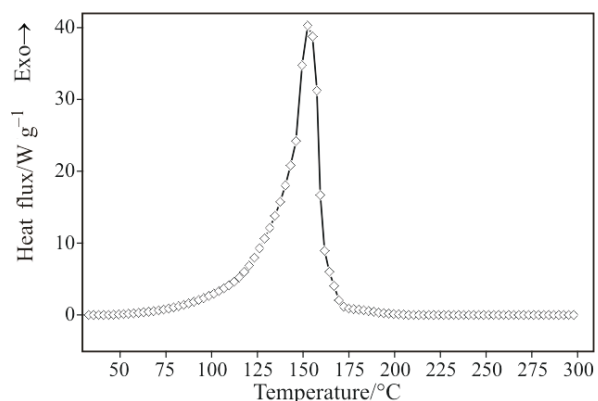


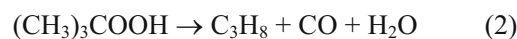
Fig. 5 Thermal curves of TBHP solutions with NH₄OH_(aq) 28 mass% by DSC trials

mena and enthalpy, and the thermal analysis data chosen from a typical trial via repeated tests are listed in Table 1.

From the experimental data, the lowest temperature of initial decomposition of TBHP solutions reacting with alkaline contaminants was

about at 40°C. This result indicates that TBHP in case of some alkaline impurities, the reactive decomposition may occur at room temperature. On the other hand, the different heats of decomposition of aqueous TBHP, TBHP/NaOH, TBHP/KOH, TBHP/LiOH, TBHP/NH₄OH and TBHP/NaCl solutions were integrated and normalized to select the incompatible hazards rating. Aside from the qualitative similarity detected in DSC dynamic thermal scanning, these adiabatic exothermic behaviors are much more quantitative in VSP2 trials. The effects of various solutions were extremely different from each other in onset temperature (T_0), self-heating rate (dT/dt), reaction maximum pressure (P_{max}) and temperature (T_{max}), pressure rising rate (dP/dt), and so on of adiabatic runaway rise. Where the potential exists for an adiabatic runaway reaction, the temperature and pressure historically behaviors that the reaction could recognize is one good measure of the magnitude of the hazard via VSP2 adiabatic calorimetric method. From quantitative and repeated trials, the characteristic curves of self-heating rate vs. reciprocal temperature and pressure behaviors for aqueous TBHP solution are recorded from Fig. 7 and the curves of temperature increasing vs. reciprocal time are delineated in Fig. 8.

The thermal curves of TBHP with various alkaline were quite different, showing that the exothermic patterns were totally variable, and numbers of exothermic peaks and heat of decomposition of TBHP with alkaline demonstrate a complicated reaction mechanism and thermal incompatible hazard, which indicates that it will result in the highest exothermic hazard in case of upset conditions. Purely TBHP thermal decomposition, for which the corresponding heat of decomposition at 25°C is about 2500 J g⁻¹ [7], and the hypothetical but energetic decomposition reaction can be expressed as follows:



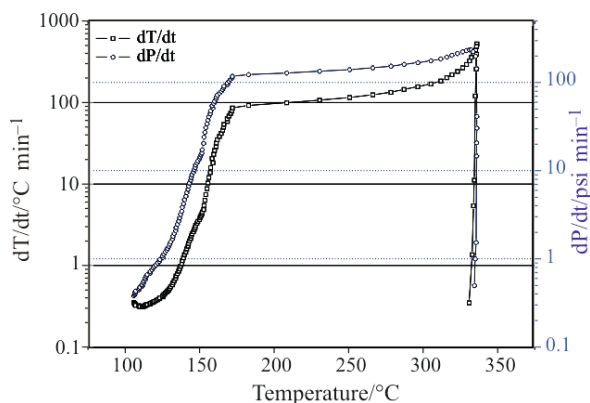


Fig. 7 Pressure rise rate and self-heating rate for thermal decomposition of aqueous TBHP 15 mass% solution

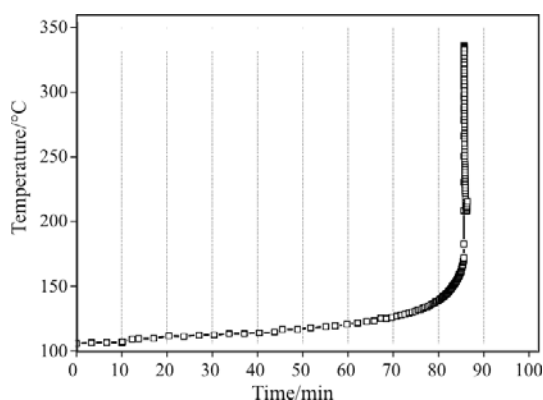


Fig. 8 Temperature-time curve in adiabatic runaway system of aqueous TBHP 15 mass% solutions

Furthermore, we could evaluate the thermal hazards of energetic chemicals by analytic equation-related adiabatic calorimetry in our previous study [10]. Two parameters, such as temperature of initial decomposition and the heat of decomposition of thermal curves by DSC [11], combined with the simplified analytical equations and the related physical properties were proposed to establish an emergency relief system.

Conclusions

Tert-butyl hydroperoxide (TBHP) is a typical alkyl hydroperoxide for commercial and industrial applications. It decomposes rapidly on heating and under influence of light and reacts violently with incompatible substances or ignition sources (acids, bases, reducing agents and heavy metals) to cause fire and explosion hazard. It should be kept away from reducing agents and incompatible substances. The calorimetric evaluation outlined above shows that TBHP solutions with alkaline have potential thermal

instability and care should be taken in shipping, handling and storing. Again in this test, we found that the contaminants play a role, although in the case of result in different thermal hazards. Nevertheless, aqueous TBHP resulted in the highest risk of thermal and self-reactive hazards. However, more severe phenomena have been discovered by calorimetry in that it will undergo thermal decomposition in the case of contaminants. This study used the preliminary calorimetry approach to identify the effect of the incompatibility on the thermal hazards of TBHP with alkaline. The adiabatic runaway test, such as VSP2 methodology, should be applied to understand the safe design and precaution the hazards of incompatibility of TBHP.

Acknowledgements

The authors thank the National Science Council of the ROC for financial support of this study under Contracts NSC 96-2628-E-224-033-MY3 and NSC 97-2922-I-224-055.

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DOI: 10.1007/s10973-008-9464-6