REACTIVE INCOMPATIBILITY OF DTBP MIXED WITH TWO ACID SOLUTIONS

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Organic peroxides are commonly employed as an initiator for polymerization, a source of free radicals, a hardener, and a linking agent. Due to its relatively weak oxygen–oxygen bond, *di-tert* butyl peroxide (DTBP) has been categorized as flammable type or Class III by the National Fire Protection Association (NFPA). The transport of dangerous goods (TDG) has published a warning against DTBP that it could potentially induce violent heat, explosion, fire and self-ignition under certain circumstances.

DTBP has been recommended as an international standard sample for estimating the performance of several calorimeters, such as glass tube tests, differential scanning calorimetry (DSC), and vent sizing package 2 (VSP2). In this study, we measured the precise temperature changes and heat flow with the above-mentioned testing instruments. However, some runaway incidents caused by DTBP have demonstrated the reaction temperature could be as low as ambient temperature. The reactivity and the hazardous incompatibility with sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) of DTBP have not been evident, and the runaway hazards involved in different processing conditions were clarified in this study by implementing the two calorimeters. Acid-catalyzed characteristics and reaction hazards of DTBP could be acquired, such as heat of decomposition (ΔH_d) and exothermic onset temperature (T_0).

Introduction

Liquid organic peroxides have been commonly employed in various industrial processes and chemical plants. *Di-tert* butyl peroxide (DTBP) is an important industrial chemical that acts as an initiator for radical polymerization, initiators, hardeners, and linking agents [1–3]. Basically, DTBP is a typical organic peroxide that is reactive to other incompatibilities and intrinsically unstable to thermal effects. The decomposition behavior is exothermic and self-ignition may occur inevitably. DTBP, which is well known and characterized organic peroxide, has always been employed as a standard sample for demonstrating the performance of calorimeters [4, 5].

In 1997 a DTBP drum explosion during a manufacturing process led to a fire that caused devastating damage and impairment. Fortunately, the immediate area affected was unoccupied at the time of the explosion and no one was injured [6]. DTBP with incompatible acid could induce an exothermic reaction at room temperature, followed by producing a large amount of heat and gas which may cause runoff, explosion, fire, and other thermal hazards [7–11]. The purpose of this study was to evaluate the incompatibility of DTBP with incompatible materials, here sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) which are employed in manufacturing processes.

Experimental

Samples

DTBP is a clear and colorless to yellow liquid substance. When used to link with other organic peroxides, it is a powerful oxidizer that reacts with reducing agents and is subject to decomposition when exposed to thermal sources.

Experimental techniques, such as preliminary estimate, glass tube tests, differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2), were proposed. Based on the experimental techniques applied, it could be determined by heat of decomposition (ΔH_d), exothermic onset temperature (T_0), thermal hazards, and the characteristics of adding H_2SO_4 and HCl to DTBP were incompatible.

Methods

Glass tube tests

A Borosilicate glass disposable culture test tube with a diameter of 16 mm and length of 150 mm was em-

ployed, and a K-type TES 1310 thermocouple with a stainless steel sheath with an outer diameter of 1.0 mm was placed at the center of the bottom. 1 mL of DTBP was placed into the test tube in a laboratory fume hood, and a thermocouple was put into the test tube in the center. Then 0.2 mL of the incompatible materials was injected into the test tube and the temperature rise was observed for 5–6 min. A digital camera was used to record the tests.

Differential scanning calorimetry

In DSC tests, a gold crucible is applied for specific applications, especially when higher temperatures and pressures are anticipated [12]. Temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821[e]; the test cell (Mettler ME-26732) could withstand high pressure to approximately 100 bar [13]. STAR[e] software was operated for acquisition of thermal curves and for analyzing chemical kinetics. Scanning rate chosen for the temperature-programmed ramp was 4°C min^{-1} to maintain a better thermal equilibrium. About 1 to 10 mg of the testing sample was selected for acquiring the experimental data. The test cell was sealed manually by a special tool equipped with Mettler's DSC, and dynamic scanning was conducted by starting the programmed setting.

Vent sizing package 2

A PC-controlled adiabatic calorimeter system, VSP2 manufactured by Fauske Associates, Inc., was employed to measure the thermokinetics and thermal hazard data, such as temperature and pressure traces with respect to time. Essentially, the low heat capacity of the cell ensures that all the reaction heat released remains within the test sample.

Thermokinetics and pressure behaviors in the accelerating rate calorimeter (ARC) bomb, therefore, can be extrapolated directly to the process scale due to the low thermal inertia about 1.45. An ARC bomb was made of stainless steel with a mass of 32 g and volume of 27 m^3. In the experimental conditions, if the self-heating rate is larger than 0.02°C min^{-1} the heat–wait–search mode and main heater should be immediately stopped for measuring the original phenomenon of self-exothermicity.

Results and discussion

Glass tube test measurements

Glass tube tests can more easily demonstrate the exothermal phenomenon, and it is simple for a screening test. The mixing test results are summarized in Tables 1 and 2. DTBP was observed to be largely exo-

Table 1 DTBP mixed with H_2SO_4 by glass tube tests

	DTBP/ mL	H_2SO_4/ mL	H_2SO_4/ N	T_0/ °C	T_{final}/ °C	ΔT/ °C
1	1.0	0.2	20.1	20.7	85.5	64.8
2	1.0	0.2	10.1	20.7	38.3	17.6
3	1.0	0.2	6.0	20.7	23.1	2.4
4	1.0	0.2	1.0	20.7	21.5	0.8

Table 2 DTBP mixed with HCl by glass tube tests

	DTBP/ mL	HCl/ mL	HCl/ N	T_0/ °C	T_{final}/ °C	ΔT/ °C
1	1.0	0.2	10.2	24.0	26.7	2.7
2	1.0	0.2	6.0	24.2	26.1	2.1
3	1.0	0.2	5.1	23.9	24.4	0.5
4	1.0	0.2	1.0	24.0	24.5	0.3

thermic when added to various concentrations of H_2SO_4, such as 1, 6, 10.1 and 20.1 N. With the increase of the H_2SO_4 concentration, the exothermic temperature (ΔT) rose too. However, the temperature only rose a few °C when HCl was added to DTBP.

DSC measurements

Toluene is the common choice as a thinner applied in various calorimeters. However, for the purpose of safety, acetone has been chosen with less toxicity and more safety. DSC testing was conducted to confirm acetone's capability to thin DTBP (Fig. 1).

From DSC dynamic scanning tests, as the dosing ratio of 98 mass% DTBP and 98 mass% H_2SO_4 was 3:2, the T_0 was reduced from 122 to 35°C. Moreover, an incompatible reaction will induce a runoff reaction at high temperatures and will lead to a worse exothermic hazard. To accurately validate the test, we lowered the concentration of sulfuric acid to 0.1, 1 and 6 N, as shown in Fig. 2.
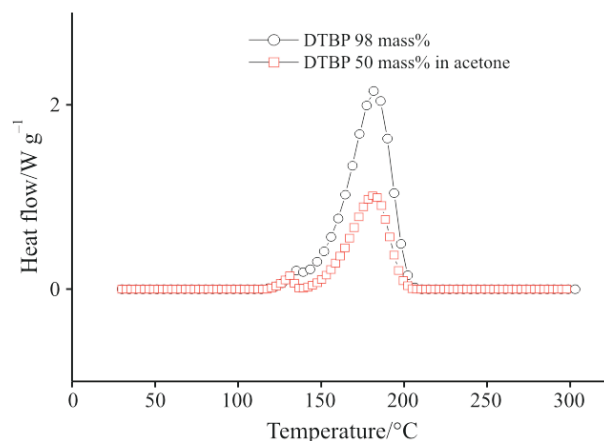

Fig 1 Thermal decomposition of DTBP 50 mass% in acetone compared to DTBP alone by DSC tests
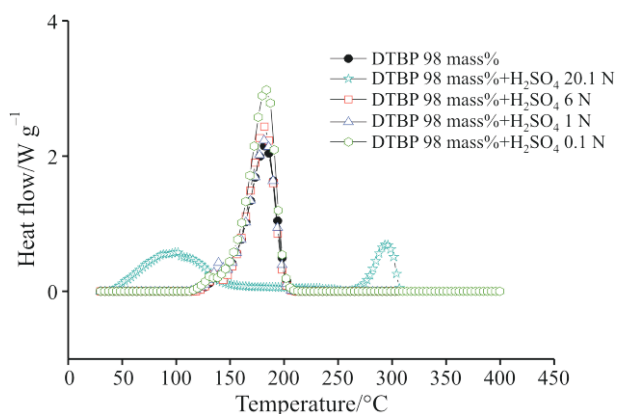
Fig. 2 Thermal decomposition of DTBP–H$_2$SO$_4$ compared to DTBP alone by DSC tests

Using DSC to analyze initial temperature being raised, this study showed that when DTBP is mixed with different substances, such as H$_2$SO$_4$ and HCl, various reactions are observed. When observing for the T_0, DTBP 25 mass% releases heat started at 145°C; however, after incompatible substances are added, the temperature at which heat already dissipated was at 35°C (H$_2$SO$_4$–20.1 N) and 88°C (HCl–10.2 N). In addition, since loss of temperature control is probable with rapid temperature rises when DTBP is contaminated or during fire, thermal explosion, or thermal hazard, such events can be the result of such a condition. In this study, the concentration of H$_2$SO$_4$ was lowered to 0.1, 1 and 6 N for T_0 observation. As displayed in the thermal curve, the initiation of T_0 was earlier with each increase of the concentration of the incompatibility. After H$_2$SO$_4$ 6 N and H$_2$SO$_4$ 1 N were individually added, the reaction index and highest reacted temperature were similar to DTBP; however, there was a difference in onset heat releases and reactive temperature. The heat release increased from 948 to 1089 J g^{-1}. During the study, the heat release that was produced increased from 948 to

1462 J g^{-1} which was an approximate increase of 500 J g^{-1}. However, the T_0 was slightly delayed: from the original 140 being delayed to 145°C. According to the general comparison of various concentrations and their premature effects, it was demonstrated in the thermal curve that the phenomenal reactions occurred early and correlated to the various H$_2$SO$_4$ concentrations. Besides, when DTBP was mixed with H$_2$SO$_4$–20.1 N the heat release was 730 J g^{-1}, a ΔH value lower than other concentrations of H$_2$SO$_4$. Before disposed the crucible into DSC, when DTBP was mixed with H$_2$SO$_4$–20.1 N. An exothermic reaction occurred immediately and heat was released to the air. Therefore, DSC only detected part of the decomposition heat.

We found that by increasing the concentration of H$_2$SO$_4$, the onset temperature quickened; as droplets of 1 and 6 N were added into crucible, heat was released instantaneously and DSC was only able to detect heat that had already been dissipated. Thus, this result demonstrated the high incompatibility and thermal hazard of DTBP with H$_2$SO$_4$. Figure 3 illustrates the incompatibility of DTBP mixed with HCl as eval-
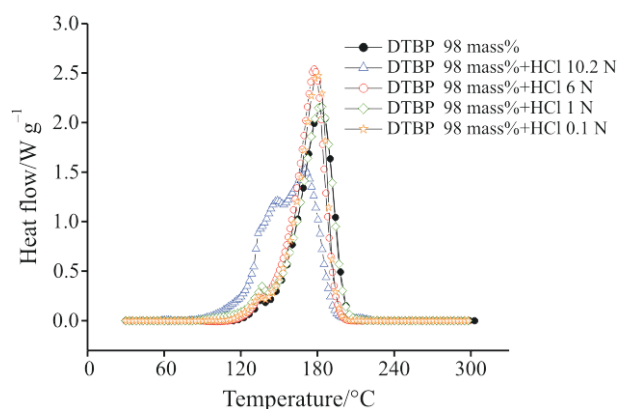

Fig. 3 Thermal decomposition of DTBP–HCl compared to DTBP alone by DSC tests

Table 3 Heat of decomposition and other parameters of DTBP 98 mass% mixed with H$_2$SO$_4$ and HCl by DSC tests

Experiment	DTBP 98 mass%	Incompatibility		T_0/ °C	1st peak temperature/°C	2nd peak temperature/°C	ΔH_d/ J g^{-1}
		Acid	Mass/mg				
1	4.00	–	–	122	181	–	948
2	2.77	H$_2$SO$_4$ 0.1 N	3.01	145	183	–	1462
3	1.99	H$_2$SO$_4$ 1 N	4.10	131	182	–	1063
4	2.91	H$_2$SO$_4$ 6 N	3.00	122	182	–	1089
5	3.60	H$_2$SO$_4$ 20.1 N	2.40	35	100	294	730
6	3.11	HCl 0.1 N	3.30	118	183	–	1065
7	3.44	HCl 1 N	3.60	113	181	–	1059
8	3.30	HCl 6 N	3.45	109	177	–	1070
9	3.81	HCl 10.2 N	4.01	81	184	–	1149

– not detectable

uated by DSC. This finding confirms the similarity in characteristics of the alleviation in concentration as in H_2SO_4. Furthermore, Table 3 summarizes the incompatible experimental data, which can be scrutinized with reliable results.

VSP2 measurements

VSP2 was employed to validate the level of thermal hazard as produced in various mixtures of DTBP with the two substances, and with a focus on the kinetic parameters including pressure, temperature, pressure rise rate (dP/dt), self-heating rate (dT/dt) and T_0. The incompatibility of DTBP with H_2SO_4 and HCl is indicated in Figs 4 to 7.

Studies have shown that when DTBP is mixed with the two substances, the increase in adiabatic temperature plateaus at a given maximum possible temperature while pressure continues to rise. This finding indicates the explosive pressure could be remarkable when temperature control may be lost. In a comparative analysis, the slightly early onset of thermal release and increase of temperature demonstrated the
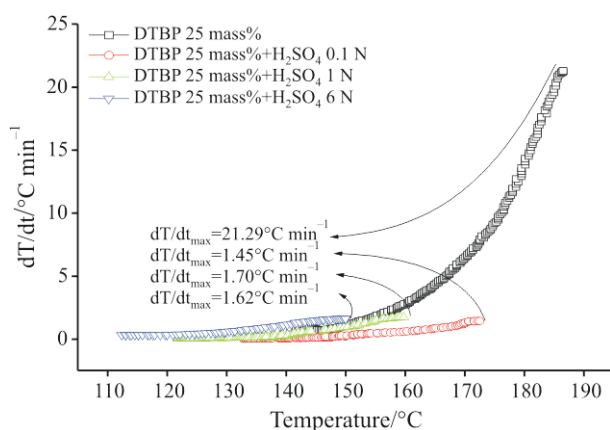

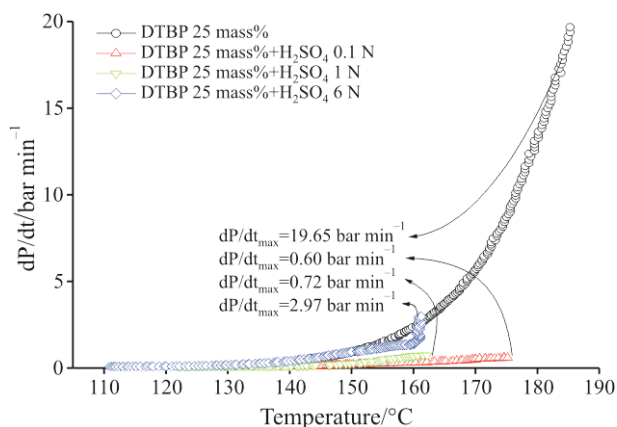**Fig. 4** Self-heating rate *vs.* temperature for DTBP–H_2SO_4 under various concentrations by VSP2 tests

Fig. 5 Pressure rise rate *vs.* temperature for DTBP–H_2SO_4 under various concentrations by VSP2 tests
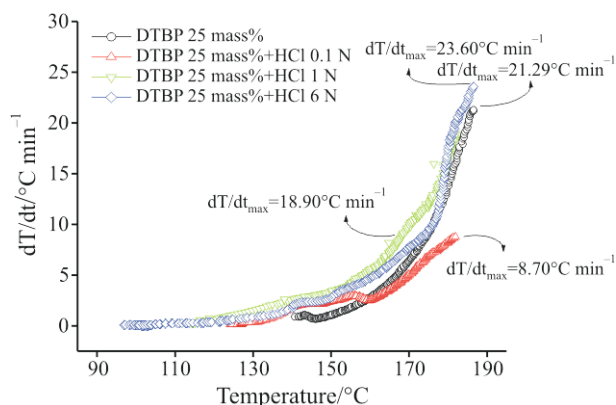

Fig. 6 Self-heating rate *vs.* temperature for DTBP–HCl under various concentrations by VSP2 tests
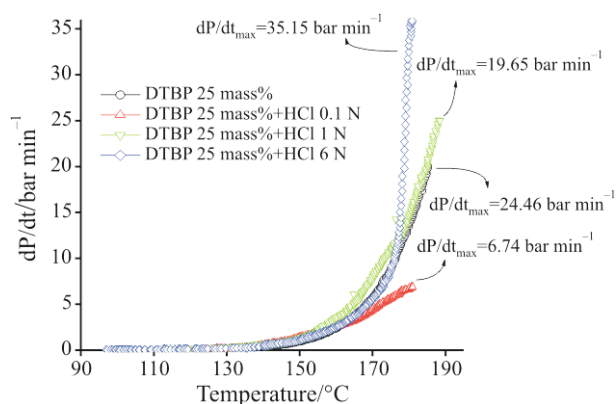

Fig. 7 Pressure rise rate *vs.* temperature experimental data for DTBP–HCl under various concentrations by VSP2 tests
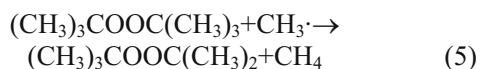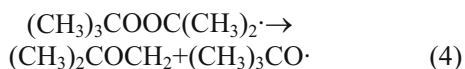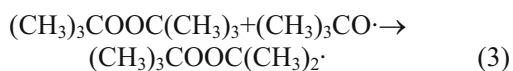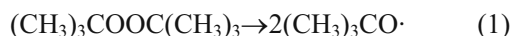
incompatibility of DTBP with H_2SO_4, while HCl illustrated a much earlier T_0. For thermal analysis of mixing DTBP with acid, this study found that when the incompatible substance H_2SO_4 was added, the runaway reaction had the highest pressure and highest temperature. On the contrary, the T_0 and pressure were relatively lower. However, due to the characteristics of the incompatibility, the increasing temperature can start earlier than predicted; therefore, the danger can be substantial even if the temperature and pressure are lower.

Initial analysis and findings on the addition of incompatible HCl could be explained as follows: there is no obvious incompatible reaction noted between DTBP and HCl; except when DSC scanning noted that when HCl was added, the onset temperature increased more rapidly. Adiabatic calorimetry VSP2 observed a change in the incompatibility from mild reaction to severe reaction. Using the heat–wait–search method, the dT/dt and dP/dt were both reaching 23.60°C min^{-1}, 35.15 bar min^{-1}. Due to the runaway reaction as a result of aggressive reaction during the high speed dT/dt and dP/dt and to protect researchers' safety as well as the equipment's capa-
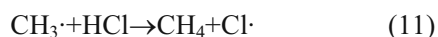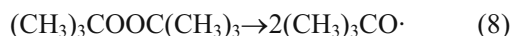
bility, the study was terminated by switching off the reactor. The probability is that dP/dt might reach 68.9 psi min^{-1} which is greater than the current index available in references. Therefore, the incompatibility was obvious in the mixture of DTBP and HCl. The unforeseen danger is beyond prediction.
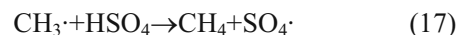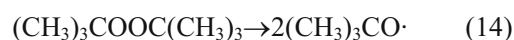
Modified mechanism

Up to now, products of adiabatic exothermic decomposition of substances have rarely been determined. The pathway of the decomposed product of neat DTBP showed the presence of acetone, *tert* butyl alcohol, and isobutylene oxide as the principal decomposition products, while a gaseous phase product analysis indicated the presence of methane and ethane [1]. A complete product analysis was not made, whereas ethyl chloride was identified again as a major component. A small amount of methane was also produced [16]. According to Schemes 1 and 2, Scheme 3 was proposed. In Scheme 3 the major reaction products, such as acetone, *tert* butyl alcohol and methane were deduced. In summary, the proposed reaction mechanisms for pure DTBP and DTBP

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \quad (1)$$

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \quad (2)$$

$$(CH_3)_3COOC(CH_3)_3 + (CH_3)_3CO\cdot \rightarrow$$
$$(CH_3)_3COOC(CH_3)_2\cdot \quad (3)$$

$$(CH_3)_3COOC(CH_3)_2\cdot \rightarrow$$
$$(CH_3)_2COCH_2 + (CH_3)_3CO\cdot \quad (4)$$

$$(CH_3)_3COOC(CH_3)_3 + CH_3\cdot \rightarrow$$
$$(CH_3)_3COOC(CH_3)_2 + CH_4 \quad (5)$$

$$2CH_3 \rightarrow C_2H_6 \quad (6)$$

$$CH_3COCH_3 + CH_3\cdot \rightarrow CH_3COCH_2CH_3 \quad (7)$$

Scheme 1 Mechanistic pathway for pure DTBP [1]

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \quad (8)$$

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \quad (9)$$

$$(CH_3)_3CO\cdot + HCl \rightarrow CH_3COCH_3 + Cl\cdot \quad (10)$$

$$CH_3\cdot + HCl \rightarrow CH_4 + Cl\cdot \quad (11)$$

$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \quad (12)$$

$$CH_3COCH_3 + CH_3\cdot \rightarrow CH_3COCH_2CH_3 \quad (13)$$

Scheme 2 Modified mechanistic pathway for DTBP with HCl [12]

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \quad (14)$$

$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \quad (15)$$

$$(CH_3)_3CO\cdot + H_2SO_4 \rightarrow (CH_3)COH + HSO_4\cdot \quad (16)$$

$$CH_3\cdot + HSO_4 \rightarrow CH_4 + SO_4\cdot \quad (17)$$

$$CH_3COCH_3 + CH_3\cdot \rightarrow CH_3COCH_2CH_3 \quad (18)$$

Scheme 3 Proposed mechanistic pathway for DTBP with H$_2$SO$_4$

in incompatible materials (HCl and H$_2$SO$_4$) as suggested by previous researchers [1, 16] and our modifications, the mechanistic pathways are delineated in Schemes 1–3. Further studies by chromatography to corroborate three reaction schemes are recommended.

Conclusions

We explored the incompatibility of the mixture of DTBP with H$_2$SO$_4$ and HCl. After repeated tests by using glass tube tests, DSC and VSP2 measuring instruments, it was evident that after acidic substances were added into DTBP, violent reactions were monitored at room temperature, even in the calorimeters. When incompatible substances HCl 0.1, 1, 6 and 10.2 N were added, the reaction order and reaction maximum temperature were the same as DTBP alone. The T_0 and heat release occurred 59°C earlier, and this explained the ratio between the T_0 and concentration. The T_0 of DTBP decreased from 140 to 81°C, accordingly. This finding confirmed that when DTBP is mixed with the incompatible HCl, the overall heat hazards are exacerbated and the occurrence of such accidents is highly dependent on the concentration of HCl.

According to the data and evidence collected in this study, it is advisable that when transporting and handling of DTBP, extra precaution should be taken to avoid contamination and mixing with incompatible materials in order to not trigger runaways, explosions and fires. For this reason the system must evaluate safety parameters such as time to maximum rate (TMR), temperature of no return (T_{NR}) and self-accelerating decomposition temperature (SADT) in the future, and even be combined with a simulation model. The whole results obtained are suitable for the study of the phenomena of runaway reactions involving pure substances or mixtures of interest.

Acknowledgements

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