



Thermal Hazard Analysis of Organic Peroxides by Adiabatic Calorimetry

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Organic peroxides are widely used in the chemical industry as initiators or curing agents for polymerization reactions. However, the use of peroxides presents an intrinsic hazard due to the presence of the highly unstable peroxy group which causes peroxides readily decompose. In present study, the thermal hazards of a selected organic peroxide, the benzoyl peroxide (BPO), were experimentally investigated by using adiabatic calorimetry. On the basis of experimental results, the thermal hazard parameters under adiabatic conditions were estimated. Preliminary data with respect to decomposition onset temperatures and decomposition heat were obtained by simultaneous TG-DSC-FTIR analysis. A Phi-Tec II adiabatic calorimeter was used to study the thermal decomposition of the selected peroxide. The experimental data obtained allowed the assessment of thermokinetic parameters. Decomposition products formed during the experimental runs were sampled and characterized by FTIR and gas chromatographic techniques. The results obtained in the present investigation could be useful for the adoption of inherently safer design in the manufacturing, handling, storage, and disposal of organic peroxides.

1. Introduction

Organic peroxides are widely used in the chemical industry as initiators or curing agents for polymerization reactions. However, the use of peroxides presents an intrinsic hazard due to the presence of the highly unstable peroxy group which causes peroxides readily decompose (Maschio et al., 2010). The thermal decomposition reaction, which is usually highly exothermic, can lead to a runaway reaction and subsequent explosion. Several accidents occurred in the past in the framework of process, transportation, storage, and final disposal of organic peroxides presented these features (Huang et al., 2013).

Therefore, in order to enhance the safety of industrial operations involving organic peroxides, an in-depth characterization of the thermal decomposition of organic peroxides is required. The assessment of the thermokinetic parameters of the decomposition reaction is crucial for the mitigation and prevention of runaway reactions and related hazards during an industrial process or various stages of operations (e.g., for the appropriate design and installation of emergency relief systems in a reactor containing or producing an organic peroxide) (Duh et al., 2008).

Adiabatic calorimetry is a technique that is used for the screening of reactive chemicals, the investigation of runaway chemical reactions, and the sizing of emergency relief vents. Adiabatic calorimeters directly simulate real process conditions, and allow data to be directly applied to process scale (Pastrenzi et al., 2014).

In present study, the thermal hazards of benzoyl peroxide (BPO) were experimentally investigated. BPO ($C_{14}H_{10}O_4$, CAS 94-36-0, chemical structure in Figure 1) is a widely used organic peroxide for industrial applications, which was involved in severe accidents occurred in the past. The thermal hazards of BPO were investigated by using adiabatic calorimetry. On the basis of experimental results, the thermal hazard parameters under adiabatic conditions were estimated.

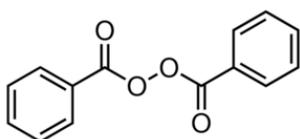


Figure 1: Chemical structure of benzoyl peroxide (BPO).

2. Past accident data analysis

Due to the high instability and reactivity, BPO is involved in many radical chemical processes, such as polymerization reactions and organic synthesis, which are among the most statistically dangerous processes (Casson and Maschio, 2012). In order to preliminarily characterize the hazards associated with BPO, past accident data analysis was carried out. Several databases and literature sources were adopted in order to trace the most relevant accidents occurred in the past. Table 1 shows the results of the analysis and the correspondent data sources. As shown in the table, the most severe accidents causing a high number of injuries and fatalities were due to process upsets or propagation of accidents due to domino effects. Therefore, the investigation of critical conditions leading to BPO decomposition is of utmost importance for the enhancement of operations safety.

Table 1: Summary of most relevant accidents involving BPO. Sources: A) MHIDAS (AEA Technology 2001); B) FACTS (UIHFD, 2016); C) http://www.sozogaku.com/fkd/en/lisen/hyaku_lisen.html; D) (Sun et al., 2012); E) (Huang et al., 2013); F) US Chemical Safety Board (<http://www.csb.gov/investigations/>); n.s. = not specified.

Year	Country	Short summary	Fatalities \ Injuries	REF
1954	Japan	Error in loading batch distillation column, explosion	0 \ 7	C
1961	USA	Explosion of vinyl acetate reactor involving BPO	1 \ 250	B
1962	USA	Explosion of BPO and other peroxides during truck unloading	4 \ 5	B
1974	USA	Explosion of BPO during road transportation	0 \ 5	B
1987	UK	Accidental leakage and fire	0 \ n.s.	B
1990	Japan	Explosion in BPO production reactor and domino effect	8 \ 17	C
1991	Japan	Explosion in BPO storage	9 \ 22	A
1992	The Netherlands	Accidental leakage and dispersion after truck overturning	0 \ 0	B
1993	China	Explosion in a food additives plant	27 \ 33	D
1995	USA	Accidental leakage and explosion during road transport	0 \ 2	A
2001	Taiwan	Thermal decomposition caused by explosion	1 \ 112	E
2003	USA	Explosion during solid BPO drying process	0 \ 0	F

3. Materials and methods

3.1 Materials

Benzoyl peroxide (75 weight %, remainder water) was supplied by Sigma-Aldrich (Milan, Italy). BPO, which appeared as white crystalline solid, was stored in a refrigerator at 4 °C, and, immediately prior to use, it was dried in a ventilated oven at 30 °C for 12 hours.

The compound was used pure in TG-DSC-FTIR tests, and in solution with toluene (Carlo Erba, Milan, Italy) in adiabatic calorimetry tests. The concentrations employed were 20, 25, 30 and 40 % by weight of BPO in toluene.

3.2 TG-DSC-FTIR tests

Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) data were obtained using a Netzsch STA 409/C thermoanalyzer. A constant heating rate of 5 °C/min was used in experimental runs, from 30 to 500 °C. Experimental runs were carried out using a purge gas flow (60 mL/min) of pure nitrogen. Typical sample weights of 5 to 10 mg, and open aluminium oxide crucibles, were employed.

TG-DSC analysis coupled with Fourier Transformed InfraRed (FTIR) spectroscopy of evolved gases was applied for the characterization of products evolved during BPO decomposition. TG-DSC-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during decomposition runs were carried out coupling a Bruker Equinox 55 FTIR spectrometer to the Netzsch STA 409/C thermoanalyzer by using a 2 mm internal diameter Teflon tube. The transfer line and the head of the TG balance were heated at a constant

temperature of 230 °C to limit the condensation of volatile products. FTIR measurements were carried out in a specifically developed gas cell heated at a constant temperature of 250 °C. A residence time of 30 s in the transfer line could be evaluated for the evolved gases, and this value was assumed as the time delay correction to be used for the comparison of TG-DSC and FTIR results. FTIR spectra were collected at 4 cm⁻¹ resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s, which is sufficient to follow the gas evolution rates characteristic of runs at heating rates of 5 °C/min. Evolved products were identified by the analysis of recorded FTIR spectra. Data on the quantities of products evolved were obtained by specifically developed calibration techniques, extensively described elsewhere (Marsanich et al., 2002).

3.3 Adiabatic calorimetry tests

A Phi-Tec II adiabatic calorimeter developed by Hazard Evaluation Laboratory was used to investigate the adiabatic decomposition of BPO. Tests were performed on solutions (6 mL) of BPO in toluene, using stainless steel cells magnetically agitated (10 mL volume), with a thermal mass of 15.23 J/K. Runs were performed in a heat-wait-search mode. A threshold of 0.02 °C/min was arbitrarily chosen as the start of the exothermic activity.

In order to allow the sampling of the gaseous products formed during experimental runs, a specifically developed sampling line was connected to the Phi-Tec device. The sampling line was equipped with a manual pressure reduction valve and a FTIR gas cell or a Tedlar bag for gas sampling. At the end of the exothermic decomposition, the test cell was cooled to ambient temperature, in order to limit the solvent concentration in the vapour phase. The residual pressure, due to the presence of gaseous decomposition products, was used to force the gas phase through the sampling line. The gas sampled in the FTIR cell or in the Tedlar bag was analysed by FTIR spectroscopy or gas chromatography (GC), respectively. A Bruker Equinox 55 spectrometer was used for FTIR analysis. GC analysis was performed using a micro-gas chromatograph Agilent 3000 equipped with two independent channels based on an injector, a column and a thermal conductivity detector. The first channel, based on a Molsieve 5A column, and using argon as mobile phase, was suitable for the determination of hydrogen, oxygen, nitrogen, methane and carbon monoxide; the second channel, based on a PLOT U column and using helium as mobile phase, was suitable for the analysis of carbon dioxide, ethane, ethylene and acetylene. Calibration data, obtained using known concentration gas mixtures of the species of interest, allowed the determination (by FTIR or GC analysis) of the molar concentration in the sampled gas of each chemical species identified. Based on the total number of gaseous moles present in the test cell during the sampling (estimated from the free volume, the pressure and the temperature of the test cell), quantitative data on gaseous products formed during adiabatic decomposition runs could be obtained.

The liquid residue present in the test cell at the end of experimental runs was collected for further chromatographic characterization.

4. Results and discussion

4.1 TG-DSC-FTIR tests

Preliminary data with respect to BPO decomposition onset temperatures and decomposition heat were obtained by simultaneous TG-DSC-FTIR analysis.

The typical results of constant heating rate TG-DSC runs performed on BPO are shown in Figure 2. The DSC curve reveals an exothermic peak, which is caused by the decomposition process, as evidenced by the weight loss curve (Figure 2a). The analysis of DSC data allowed an estimation of the onset temperature and of the thermal effects of the decomposition process. The onset temperature resulted of 108.5°C at a heating rate of 5°C/min. The exothermic effect of BPO decomposition was evaluated to be of 1260 J/g. Heat of decomposition and onset temperature values obtained in the present study are in good agreement with those reported in the literature for DSC runs carried out on BPO samples using a heating rate of 4 °C/min and sealed high pressure crucibles. As a matter of fact, Duh et al. (2008) reported an onset temperature of 105°C and an exothermic decomposition heat of 1034 J/g; Wu et al. (2012) indicated an onset temperature of 103°C and a decomposition heat of 1332 J/g. Onset temperature and decomposition heat values of 102 °C, 98 °C, 106 °C, and 1045 J/g, 990 J/g, 1178 J/g, were reported for 75 weight % BPO by Tsai et al. (2012), Lee et al. (2014), and Lee et al. (2015), respectively.

Among gaseous decomposition products, the formation of carbon dioxide was revealed by the simultaneous FTIR analysis of evolved gases. Figure 2b shows the emission profile of carbon dioxide compared with the sample weight loss rate curve. A strong correspondence is observed between the emission of carbon dioxide and the exothermic decomposition step. The results of the quantitative analysis of evolved gases indicated the formation of 18 g of CO₂ per 100 g of sample, which corresponds to 1.0 mol of carbon dioxide per mol of BPO.

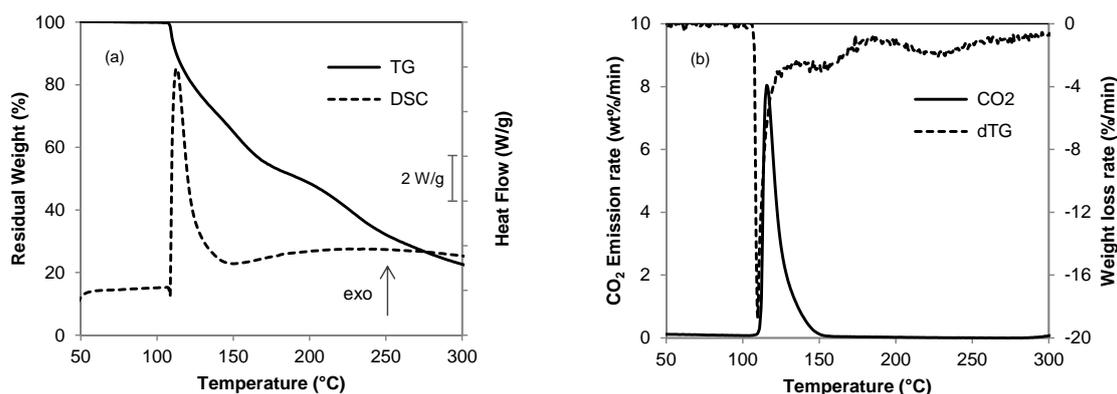


Figure 2: Results of TG-DSC-FTIR runs performed on BPO (5 °C/min heating rate, 100% nitrogen). a) Weight loss and heat flow curves. b) Emission profile of carbon dioxide and weight loss rate curve.

As a matter of fact, the BPO decomposition reaction mechanism reported in the literature involves homolysis of the O–O bonding and radical-induced decomposition, with formation of carbon dioxide and biphenyl as final degradation products, along with smaller amount of phenyl benzoate and benzene (Sun et al., 2012).

4.2 Adiabatic calorimetry tests

The exothermic decomposition of BPO was studied performing experimental runs with the Phi-Tec calorimeter on BPO solutions in toluene with concentration ranging from 20 to 40 % by weight. Typical temperature and pressure profiles inside the reactor are plotted in Figure 3.

The analysis of the temperature rise during experimental runs allowed the estimation of the adiabatic temperature rise and of the heat of reaction of BPO by standard procedures (CCPS, 1995). A summary of the results obtained for BPO solutions of different concentrations is shown in Table 2. The table includes the values obtained for the decomposition onset temperature as well. Lower onset temperatures and higher thermal effects were recorded with respect to those measured in TG-DSC runs. Lower onset temperatures were recorded in the present study with respect to those reported in the literature for the decomposition of BPO in Accelerating Rate Calorimeter (ARC) and vent sizing package 2 (VSP2) tests: onset values of 94 °C, 92.4 °C, and 90 °C were reported by Tsai et al. (2012), Sun et al. (2012), and Pasturenzi et al. (2014), respectively. A similar value was reported for the exothermic decomposition heat (1840 J/g) by Pasturenzi et al. (2014) (ARC test).

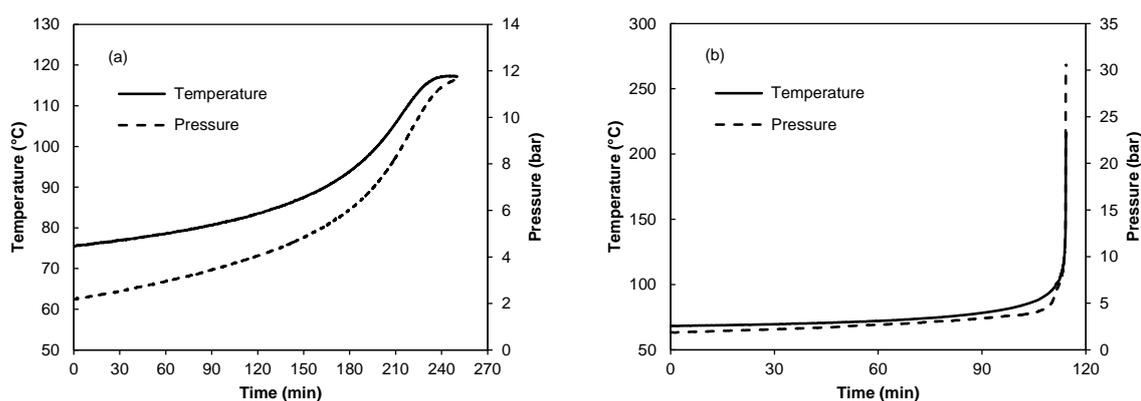


Figure 3: Temperature and pressure profiles during adiabatic decomposition tests performed on BPO. a) 20 weight % BPO solution in toluene. b) 40 weight % BPO solution in toluene.

Table 2: Results of the adiabatic decomposition runs carried out in the Phi-Tec calorimeter on BPO solutions.

BPO (weight %)	Test	T _{onset} (°C)	T _{max} (°C)	P _{max} (bar)	(dT/dt) _{max} (°C/min)	(dP/dt) _{max} (bar/min)	ΔH _{decomposition} (J/g _{BPO})
20	a	75.5	117.4	11.7	0.56	0.12	1060
20	b	78.6	118.3	11.4	0.61	0.13	1006
25	a	72.1	139.8	15.2	5.41	1.09	1356
25	b	72.1	135.2	14.6	3.37	0.73	1266
30	a	70.5	173.5	21.6	112.0	29.2	1693
30	b	70.5	173.4	21.0	108.9	25.5	1705
40	a	68.2	216.0	30.6	413.2	92.3	1768
40	b	70.7	222.0	30.0	609.1	127.8	1826

The temperature and pressure rise rates recorded for a 20 weight % BPO solution in toluene are reported in Figure 4, while Figure 5 shows temperature and pressure rise rate data obtained in experimental runs carried out on different concentration BPO solutions. The results reported in Figures 4 and 5 evidence that the BPO concentration greatly affects the maximum self-heating rate and pressure rise rate. The maximum temperature rise rate ranged from 0.6 °C/min for 20 wt % BPO to 609 °C/min for 40 wt % BPO (Table 2). A similar behaviour was observed for the pressure rise rate. Maximum rates as high as 128 bar/min were recorded for 40 % wt BPO (Table 2).

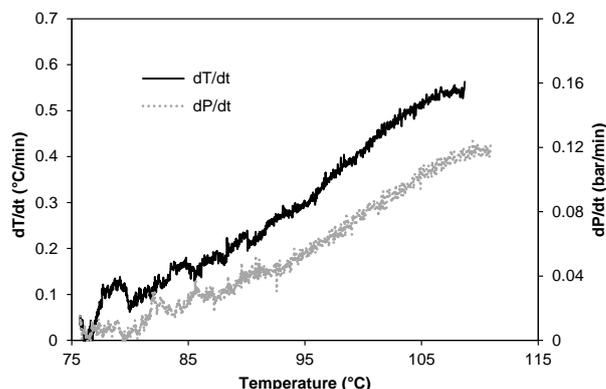


Figure 4: Temperature and pressure rise rates during an adiabatic decomposition test performed on a 20 weight % BPO solution in toluene.

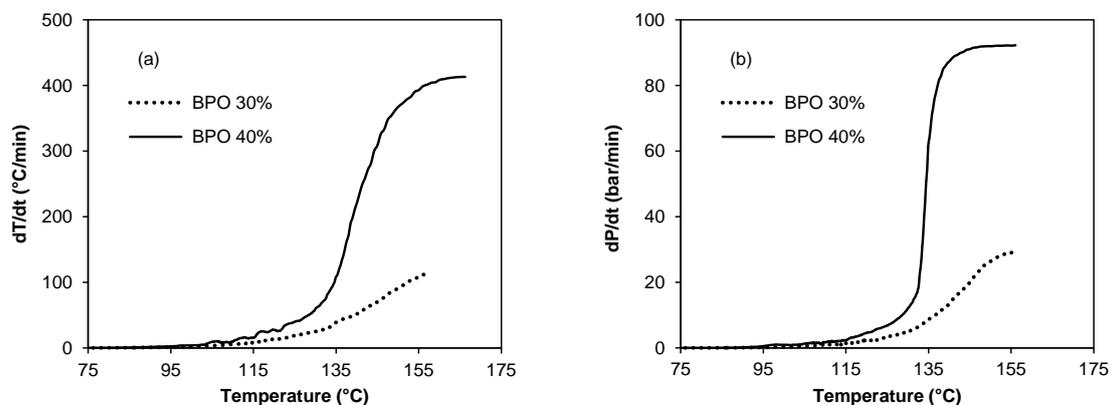


Figure 5: Results of adiabatic decomposition runs performed on BPO solutions using the Phi-Tec calorimeter. (a) dT/dt data. (b) dP/dt data.

Among gaseous decomposition products, the formation of carbon dioxide was revealed by FTIR analysis and/or GC analysis in all the experimental tests performed in the present study. The results of the quantitative determination indicated the formation of 0.28 mol of carbon dioxide per mol of BPO.

5. Conclusions

Organic peroxides feature high reactivity and instability leading the safety issues in transport, storage and process phases. The present analysis focused on the experimental characterization by adiabatic calorimetry of benzoyl peroxide (BPO). BPO is a reactant that is widely applied in industrial processes and was involved in severe accidents occurred in the chemical and process industry. A specific past accident data analysis allowed for a preliminary screening of the safety issues associated with this compound and its utilization.

Preliminary data with respect to decomposition onset temperatures and decomposition heat were obtained by simultaneous TG-DSC-FTIR analysis. A Phi-Tec II adiabatic calorimeter was used to study the thermal decomposition of solutions of BPO at different concentrations. The experimental data obtained allowed the assessment of thermokinetic parameters. Decomposition products formed during the experimental runs were sampled and characterized by FTIR and gas chromatographic techniques. The results evidence that the concentration of BPO in the solution strongly affects the decomposition rate.

The results obtained may be adopted in order to size and design the emergency discharge system aimed at the protection from overpressure of BPO storage and handling equipment. Moreover, the outcomes of this work may support further studies adopting cells featuring low thermal inertia factor (namely, Φ factor), in order to allow for a bench scale simulation of critical decomposition scenarios in the operations and storage of BPO solutions, i.e. associated with the exposure to external heat sources. Therefore, the present investigation may support the adoption of inherently safer design in the manufacturing, handling, storage, and disposal of organic peroxides.

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