Thermal decomposition of cumene hydroperoxide in the presence of three incompatible substances by isothermal microcalorimetry and high performance liquid chromatography

Y.-P. Chou · H.-Y. Hou · R.-H. Chang · M.-L. You · J.-Y. Peng · C.-M. Shu

Abstract Cumene hydroperoxide (CHP) and its derivatives have caused many serious explosions and fires in Taiwan as a consequence of thermal instability, chemical contamination, and even mechanical shock. It has been employed in polymerization for producing phenol and dicumyl peroxide (DCPO). Differential scanning calorimetry (DSC) was used to analyze the thermal hazard of CHP in the presence of sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and sodium bisulfite (Na_2SO_3). Thermokinetic parameters for decomposition, such as exothermic onset temperature (T_0), maximum temperature (T_{max}), and enthalpy (ΔH), were obtained from the thermal curves. Isothermal microcalorimetry (thermal activity monitor, TAM) was employed to investigate the thermal hazards during CHP storage and CHP mixed with NaOH, H_2SO_4, and Na_2SO_3 under isothermal conditions in a reactor or container. Tests by TAM indicated that from 70 to 90 °C an autocatalytic reaction was apparent in the thermal curves. According to the results from the TAM test, high performance liquid chromatography (HPLC) was, in turn, adopted to analyze the result of concentration versus time. By the Arrhenius equation, the activation energy (E_a) and rate constant (k) were calculated. Depending on the process conditions, NaOH was one of the incompatible chemicals or catalysts for CHP. When CHP is mixed with NaOH, the T_0 is induced earlier and the reactions become more complex than for pure CHP, and the E_a is lower than for pure CHP.

Keywords Cumene hydroperoxide ·
Differential scanning calorimetry ·
High performance liquid chromatography ·
Thermal activity monitor · Thermokinetic parameters

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Introduction

Hydroperoxides are sensitive to thermal sources, contamination, and multivalent metal ions to the extent that trace exposures could result in explosive reactions. Many earlier studies have analyzed and employed various aspects of the thermal hazard behaviors and kinetic data of CHP reactions. Incompatible reactions leading to complicated features, such as lower exothermic onset temperature (T_0), various reactions and adiabatic temperature rise (ΔT_{ad})

from the first peak, can trigger a thermal runaway or explosion [1, 2]. Concerted efforts to understand the runaway reaction for cumene hydroperoxide (CHP) in the presence of sodium hydroxide (NaOH), sulfuric acid (H$_2$SO$_4$), and sodium bisulfite (Na$_2$SO$_3$) have been made.

CHP has generally been employed to produce phenol and dicumyl peroxide (DCPO), which is used as an initiator in polymerization, especially for acrylontrile-butadiene-styrene (ABS) copolymer [3, 4]. First, the thermal hazard for CHP, which is one of the typical organic peroxides, was analyzed. The reaction of CHP while mixed with an incompatible chemical, i.e., NaOH, in the petrochemical process was, in turn, investigated. Differential scanning calorimetry (DSC) was employed to evaluate the thermal hazard for CHP compared with that for CHP in the presence of NaOH, H$_2$SO$_4$, and Na$_2$SO$_3$, individually. Thermokinetic data, such as exothermic onset temperature (T_0), peak temperature (T_{max}), and enthalpy (ΔH), were obtained using calorimetry methodology [5, 6]. Experimental data were obtained by DSC. Then, a thermal activity monitor (TAM) was used to evaluate the thermal hazards during storage of CHP and CHP mixed with three incompatible substances, NaOH, Na$_2$SO$_3$, and H$_2$SO$_4$, under isothermal conditions. NaOH is one of the incompatible chemicals or catalysts for CHP decomposition, depending on the process conditions. According to the DCPO manufacturing process, CHP, cumyl alcohol (CA), and acid are used in manufacturing DCPO. However, NaOH has been employed to neutralize excessive acid. CHP may mix with excessive NaOH leading to incompatibly circumstances [7].

In view of loss preventions, by regulation, the United Nations (UN) has suggested that an organic peroxide supplier must perform a precise test of the self-accelerating decomposition temperature (*SADT*) in any specific commercial package [8]. CHP has been recognized as flammable type or class III (fire hazard) by NFPA (National Fire Protection Association) [9].

Experimental

Materials

Cumene hydroperoxide (CHP) of 80 mass%, NaOH of 99 mass%, Na$_2$SO$_3$ of 96 mass%, and H$_2$SO$_4$ of 96 mass% were purchased directly from the supplier and then stored in a 4 °C environment. Here, NaOH, Na$_2$SO$_3$, and H$_2$SO$_4$ were treated as an incompatible chemical of interest.

Differential scanning calorimetry (DSC)

Calorimetry was accomplished with a Mettler TA8000 DSC 821^e system which can acquire the heat flow for CHP

and the composition products of heat flow. In the beginning of reaction, the thermal decomposition phenomenon was determined. The heating rate was set at 4 °C min^{-1} with a range of 30–300 °C [10–12].

Thermal activity monitor (TAM)

Isothermal microcalorimetry represents a range of products for thermal measurements manufactured by Thermometric AB in Sweden. Reactions can be investigated within 12–90 °C, the working temperature range of the thermostat. The most prominent products are highly sensitive microcalorimeters for stability testing of various types of reactive materials [13, 14]. Measurements were conducted isothermally in the temperature range of 70 to 90 °C [2, 15, 16] by TAM.

High performance liquid chromatography (HPLC)

The HPLC instrument consists of a reservoir of mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by injecting a plug of the sample mixture onto the column. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase. The presence of analytes in the column effluent is recorded by detecting a change in refractive index, UV–VIS absorption at a set wavelength, fluorescence after excitation with a suitable wavelength, or electrochemical response. Mass spectrometers can also be interfaced with liquid chromatography to provide structural information and help identify the separated analytes. Column XDB-C18, 4.6 mm × 250 mm (5 μm), and UV detection at 254 nm were used in this study [13, 17].

Theory (Arrhenius equation)

The background and theoretical development of the equations used to determine thermodynamic and kinetic parameters from isothermal heat conduction calorimetry have been discussed previously. An estimate of the degradation rate can be obtained from the Arrhenius equation:

$$k = Ae^{-Ea/RT} \tag{1}$$

In Eq. 1, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature.

Results and discussion

Possibly contaminated NaOH and H$_2$SO$_4$ were chosen as incompatible materials for 80 mass% CHP. CHP was
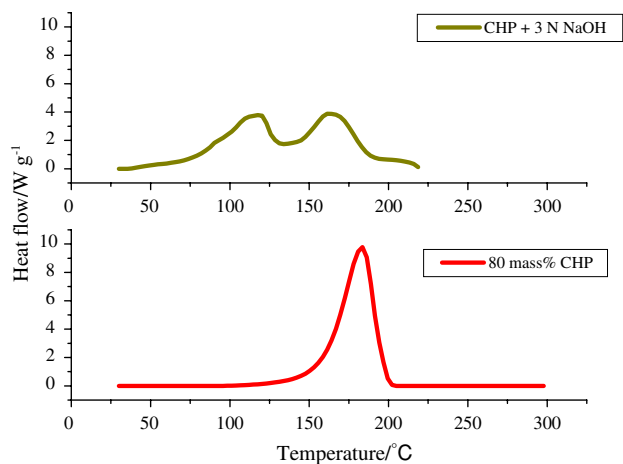
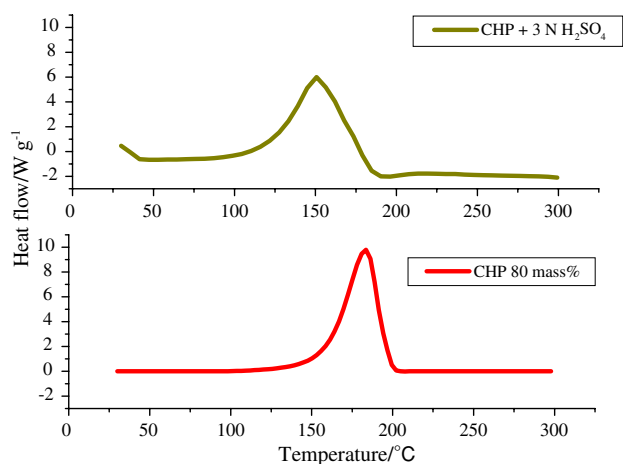**Fig. 1** Thermal curve for 80 mass% CHP admixture of 3 N NaOH by DSC with dynamic scanning rate of 4 °C min^{-1}

Fig. 2 Thermal curves for 80 mass% CHP admixture of 3 N H$_2$SO$_4$ by DSC with dynamic scanning rate of 4 °C min^{-1}

heated to the exothermic onset temperature, followed by mixing with NaOH$_{(aq)}$ and mingling H$_2$SO$_{4(aq)}$, and finally the heating step was terminated. From DSC data were determined the basic thermokinetic data of CHP in the

Table 1 Scanning data of the thermal decomposition for four samples by DSC

Sample	T_0/°C	T_{max}/°C	ΔH_d/J g^{-1}
CHP (80 mass%)	80.00	163.60	1,152.75
CHP(80 mass%) + NaOH (3 N)	40.00	98.25	826.37
CHP (80 mass%) + H$_2$SO$_4$ (3 N)	53.00	151.06	1,346.45
CHP (80 mass%) + Na$_2$SO$_3$ (3 N)	137.91	164.00	1,185.24

presence of NaOH and H$_2$SO$_4$, such as ΔH_d, T_0, and T_{max}. Figures 1 and 2 depict the thermal curves for the decomposition of 80 mass% CHP mixed in the presence of H$_2$SO$_4$ and NaOH.

The T_0 for CHP was about 80 °C, and the ΔH_d was about 1,153 J g^{-1}. The experimental data are displayed in Table 1. When CHP was mixed with H$_2$SO$_4$, the T_0 was reduced from 80 to 53 °C, and the ΔH_d was increased from 1,153 to 1,346 J g^{-1}. The hazard for CHP was less than that for CHP containing H$_2$SO$_4$. When CHP was mixed with NaOH, the T_0 was reduced from 80 to 40 °C, and the exothermic response varied from single to twin peaks. The T_0 for the first peak of the exothermic was about 40 °C, triggering the second (main) peak for the exothermic to appear earlier.

From Table 2 and Fig. 3, depending on the process operating conditions, while CHP was mixed with NaOH, the time to maximum rate (*TMR*) was significantly decreased from 3.7074 to 0.0139 days, and the highest heat flux was increased from 2.64 to 32.87 mW g^{-1} at 90 °C. When CHP was mixed with H$_2$SO$_4$, the TMR was decreased to 2.2740 days, and the highest heat flow was increased to 9.94 mW g^{-1}. The hazard increased as reflected by lower E_a and *TMR* for the process.

Figure 4 shows the thermal curves for isothermal decomposition of CHP in 70–90 °C and the thermal curves for CHP decomposition in the presence of NaOH. Here, Figs. 4 and 5 indicate that when the temperature was reduced from 90 to 70 °C, the reaction time was correspondingly increased. The thermal curves for the

Table 2 Scanning data of the thermal decomposition for three samples by TAM

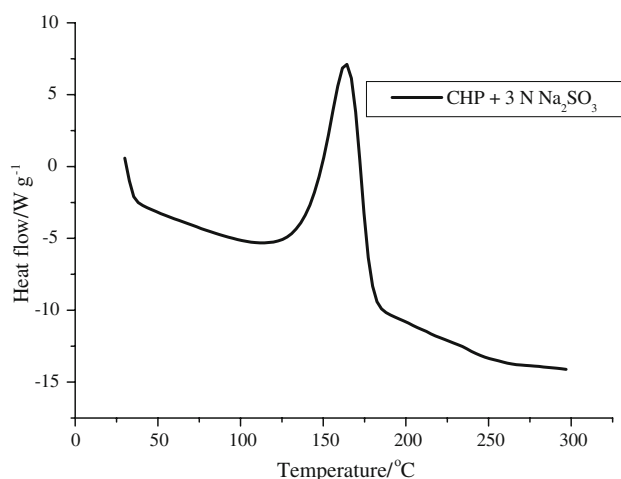| Sample	Temperature/°C	*TMR*/day	Highest heat flow/W g^{-1}	Reaction time/day
CHP (80 mass%)	70	39.2084	0.41	68.97
	80	11.9514	1.25	29.94
	90	3.7074	2.64	9.63
CHP (80 mass%) + NaOH(3 N)	70	0.0208	2.80	90.31
	80	0.0139	30.73	40.84
	90	0.0139	32.87	14.88
CHP (80 mass%) + H$_2$SO$_4$(3 N)	80	5.5354	14.56	9.92
	90	2.2740	15.94	9.26
	100	0.4082	64.87	3.78

Fig. 3 Thermal curves for 80 mass% CHP admixture of 3 N Na_2SO_3 by DSC with dynamic scanning rate of 4 °C min^{-1}

Fig. 4 Thermal curves for 80 mass% CHP by TAM at 70, 80 and 90 °C

Fig. 5 Thermal curves for 80 mass% CHP and 3 N NaOH by TAM at 70, 80 and 90 °C
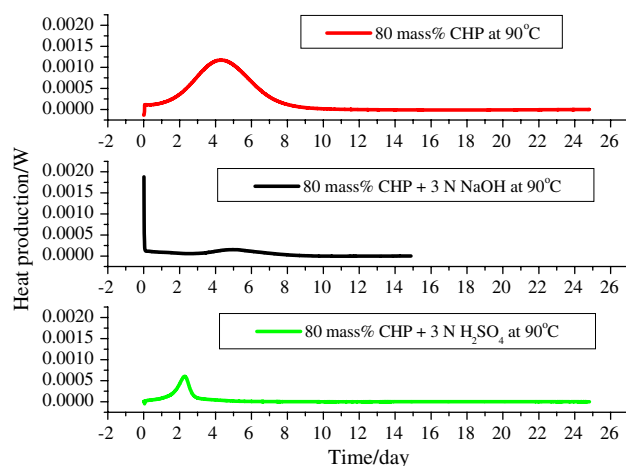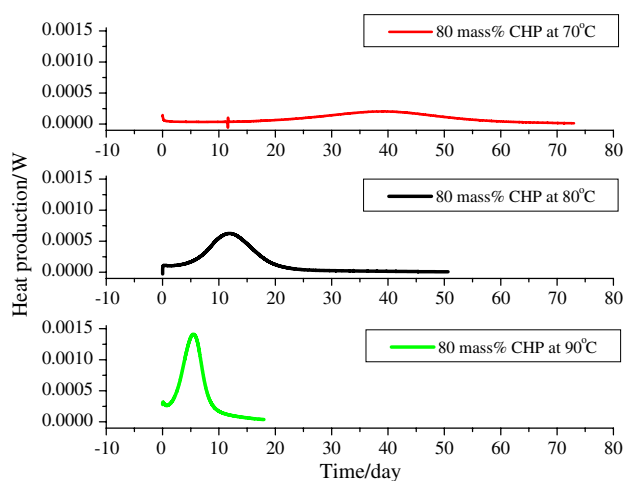

Fig. 6 Thermal curves for 80 mass% CHP with two incompatible substances, NaOH and H_2SO_4, by TAM at 90 °C

Fig. 7 Thermal curves for 80 mass% CHP and 3 N H_2SO_4 by TAM at 80, 90 and 100 °C
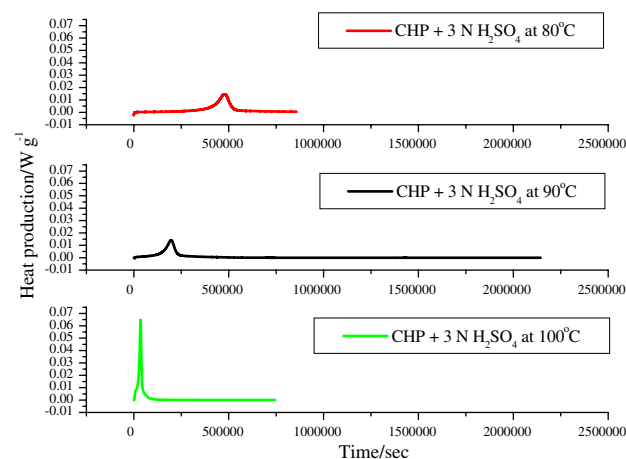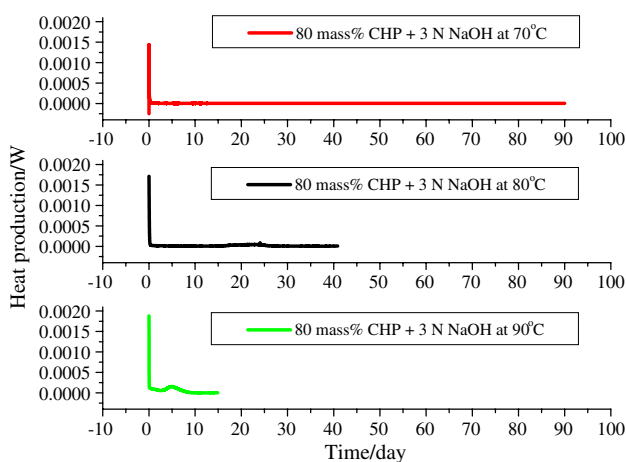
decomposition of 80 mass% CHP in the presence of two incompatible substances are in Fig. 6. Figure 7 shows the thermal curves of CHP and CHP mixed with H_2SO_4. In Fig. 8 when the temperature was reduced from 90 to 70 °C, the concentration of CHP was correspondingly decreased. The reaction time for CHP mixed with H_2SO_4 was less than others. When CHP was mixed with NaOH, the exothermic peak was altered from single to twin peaks. The same result was shown in both DSC and TAM experiments. This phenomenon was validated to be reproducible. In Fig. 6, when a sample was fed into the instrument under isothermal condition, the exothermic reaction began immediately. Figure 8 indicates that when the temperature was reduced from 90 to 70 °C, the reaction time was correspondingly increased. It confirmed that CHP mixed containing NaOH became even more dangerous than CHP alone and CHP mixed with H_2SO_4.
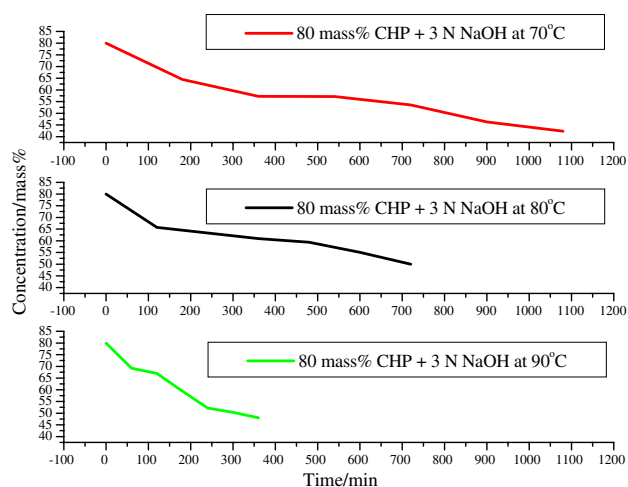
Fig. 8 Concentration profiles for 80 mass% CHP with NaOH by HPLC under 70, 80 and 90 °C

Conclusions

In manufacturing processes, DCPO is produced from CHP, CA, and acids (such as H_2SO_4). The thermal hazards of CA and acid are not as prominent as CHP and could be neglected. The hazard rating of DCPO is less than that for CHP. In the process, the main hazard was ascribed to CHP, and CHP mixed with incompatible chemicals, especially acids. To control the acidity, NaOH was mixed in this process. Nonetheless, NaOH was incompatible with CHP, as if an excess of NaOH caused the hazard by human error or poor training. The excess of NaOH was incompatible with CHP. The T_0 of CHP was reduced, and the exothermic peak of CHP was altered from single to twin peaks.

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