Exothermic Decomposition of Cumene Hydroperoxide at Low Temperature Conditions

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Fires or explosions caused by the thermal runaway of organic peroxides have been important issues in Taiwan during the past two decades (Ho et al., 1998). Calorimetry and the related methodology for preventing reactive hazards of organic peroxides have been widely developed (Duh, 1997, 1998). DIERS technology has also been useful for the safe venting of runaway reactions caused by organic peroxides in the early stages of a runaway reaction (Leung and Fisher, 1998). In a homogeneous two-phase flow case, vent sizing depends directly on the self-heating rate, which is influenced by the reaction mechanism during decomposition of the peroxides. To apply DIERS methodology for sizing an emergency vent, a credible worst-case scenario must be estimated. Thermal decomposition, external fires in tank yards, and reactive incompatibility in addition to other scenarios should be considered as the design basis for preventing runaway reactions or for sizing emergency relief.

Cumene hydroperoxide is used as an initiator in the acrylonitrile-butadiene-styrene polymerization process, for producing phenol or dicumyl hydroperoxide. Runaway incidents can occur in oxidation reactors, vacuum condensation reactors, or storage tanks. The National Fire Protection Association (NFPA 43B) (1986) classifies cumene hydroperoxide as a class III type flammable. Duh et al. have studied the runaway hazard and decomposition kinetics for various process conditions (Ho et al., 1998; Duh et al., 1998). However, the reactive characteristics of cumene hydroperoxide under storage or transport conditions have not yet been clearly identified.

Previous studies have shown that the onset temperature is 100°C for 80 wt. % cumene hydroperoxide by a differential scanning calorimetry (DSC) test (Duh et al., 1998) and 140°C for 35 wt. % cumene hydroperoxide by VSP2 (Vent Sizing Package 2) (Shu et al., 1999; Wang et al., 2001). Onset temperature is strongly influenced by the mass- and heat-releasing power of the reactant and by the sensitivity of the various calorimeters. The onset temperature for a recognized runaway reaction reported in the open literature is the temperature at which the reaction was initially detected. In this study, a microcalorimeter was used to detect and record the exothermic activity of cumene hydroperoxide under isothermal conditions in the temperature range from 75°C to 90°C. Under such conditions, conventional calorimeters, such as the DSC, or adiabatic calorimeters, such as VSP2, do not detect the heat release of cumene hydroperoxide. Exothermic thermograms were recorded with the microcalorimeter in isothermal tests which typically required about 20 days. The heat of reaction, onset temperature, and autocatalytic behaviors were determined and compared to the results of previous studies.

Experimental Studies

Sample

An 80 wt. % solution of cumene hydroperoxide in cumene purchased directly from the supplier was measured to determine both density and concentration. The sample was then stored at 4°C.

Differential scanning calorimetry (DSC)

Dynamic screening experiments were performed on a Mettler TA8000 system coupled with a DSC 821 measuring cell that can withstand pressures as high as 100 bar. Star software was used for aquiring thermograms and isothermal traces. The scanning rate for the temperature-programmed ramp was chosen to be $4\ \text{K}\cdot\text{min}^{-1}$ to attain a better approach to thermal equilibrium.

Thermal activity monitor

The heat conduction calorimeter (thermal activity monitor, Thermometric AB, Jarfalla, Sweden) is designed to monitor a wide range of chemical and biological reactions. Reactions can be investigated between 12°C and 90°C, which is the

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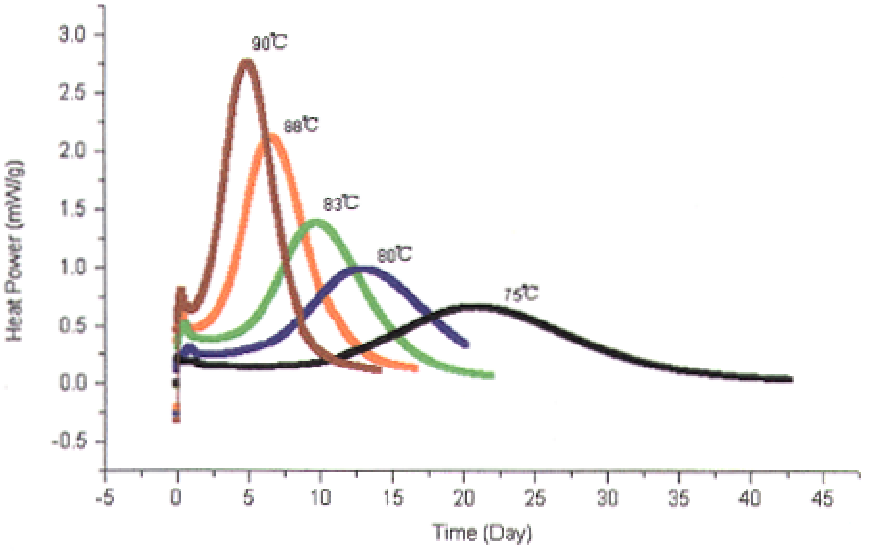

Figure 1. Heat power vs. time for thermal decomposition of 80 wt. % cumene hydroperoxide under various isothermal conditions.

working temperature range of this calorimeter. Constant temperature is maintained within $\pm 2\times 10^{-4}$°C, which allows heat flow in fractions of a micro Watt (μW) to be routinely measured. The 80 wt. % cumene hydroperoxide was dispensed into diposable calorimetric glass and stainless containers, which were capped and then placed in the measuring and reference chambers, respectively. Measurements were conducted isothermally from 75°C to 90°C.

Results and Discussion

Thermal analysis

Isothermal aging tests offer the advantage of thermal equilibrium within the reactant, which can generate more precise kinetics and simple interpretation. These tests are applicable to complex reactions such as decomposition, oxidation, and polymerization. Plots of residual cumene hydroperoxide concentration vs. time are used to determine isothermal kinetics. All of these experiments were performed between 75°C to 90°C using the microcalorimeter under isothermal conditions.

Calorimetric measurements of the slow reactions reported here have a time history from 10 days to 43 days for individual experiments. Thermograms of 80 wt. % cumene hydroperoxide that reacted in the thermal activity monitor at five different temperatures were recorded and shown in Figure 1. Table 1 lists the experimental data from the autocatalytic decomposition of 80 wt. % cumene hydroperoxide. The data show that the exothermic traces were independent of the mass effect and that the heat releasing curves were almost equal in both the glass and the steel test cells. Peak powers of these exothermic curves were from 0.5 to 2.0 mW, which is practically the noise level of the DSC and the adiabatic calorimeter, and therefore could not be detected by using these two apparatus. Heat of reaction was determined to be about 1,200 ± 50 J/g (80 wt. % cumene hydroperoxide).

Table 1. Experimental Data of Autocatalytic Reaction on CHP Conducted by TAM

Sample	Temp. (°C)	Sample Mass (g)	Cell	React. Time (d)	Time to 1st Peak (h)	ΔH of 1st Peak (J/g)	Time to 2nd Peak (d)	ΔH of 2nd Peak (J/g)
CHP 80 wt. %	90	0.506	G[*]	14.1	7.55	2.61	4.9	1,248.45
		1.511	G	16.6	11.7	3.79	6.7	1,214.49
	88	1.008	G	15.0	11.2	4.32	6.5	1,181.65
		0.504	G	16.5	8.3	4.46	6.5	1,243.41
		0.501	S	15.2	8.0	9.18	6.6	1,217.43
	83	0.510	G	22.0	13.3	6.29	9.7	1,128.86
	80	1.020	G —	20.0 (Uncompleted)[**]	20.8	4.05	13.0	980.98
	75	0.505	G	42.7	27.6	5.28	20.9	1,082.50

[*] G = glass ampoule; S = stainless steel ampoule.
[**] Power shortage due to the September 21, 1999 Taiwan earthquake.

Table 2. Thermal Analysis Data Detected by Various Calorimeters*

Calorimeter	CHP Conc.	Onset Temp. (°C)	ΔH (J/g)	Kinetics
DSC	80 wt. %	100	1,425	*n*th order
DSC	35 wt. %	135	607.3	*n*th order
ARC	35 wt. %	101.2	607.3	*n*th order
VSP2	15 wt. %	115.1	—	*n*th order
TAM (this work)	80 wt. %	75	1,200 ± 50	Autocatalytic

*From Duh (1997, 1998) and Shu (1999).

Around 20% of the heat of reaction was not delivered in the low-temperature isothermal tests, in comparison to the heat of decomposition of 1,500 J/g (80 wt. % cumene hydroperoxide) determined by DSC (Duh et al., 1997). Residual enthalpy can be detected by using temperature-programmed scanning in the DSC. The thermal analysis data were comparable to the previous studies which are presented in Table 2.

Obviously, attention is drawn to the first peak. It also appeared to be a small shoulder in DSC temperature program scanning which occurred at about 80–90°C. Di-tert-butyl peroxide (DTBP) and dicumyl hydroperoxide also displayed the first small peak in DSC experiments (Leung, 1994). However, no discrete small peaks were observed in adiabatic self-heating data.

Cumene hydroperoxide masses and experimental temperatures were varied and a cumene blank test was run to try to understand the source or the first peak. The pure cumene blank test did not exhibit the exothermic behaviors seen in the cumene hydroperoxide decomposition experiments. Table 1 shows that the heat of reaction in the first peak is less than 1% of the overall heat of decomposition. Therefore, it is considered to have relatively little influence on the overall kinetics. Possible explanations for the first peak include: (1) Recombination reaction of radicals decomposed from cumene hydroperoxide; (2) Oxidation reaction on cumene hydroperoxide (Griffiths and Mullins, 1984); and (3) Vapor phase decomposition of cumene hydroperoxide (Show and Pritchard, 1968).

Autocatalytic Behaviors

Autocataytic reactions are considered to be hazardous because of unexpected initiation and sudden heat evolution even in an isothermal environment. Isothermal calorimeters can be utilized to investigate whether a reaction is autocatalytic or *n*th-order kinetics. An autocatalytic effect is verified by a maximum rate of heat release at about 40–60% conversion of the reactant in the isothermal thermogram; whereas, the maximum rate of heat release in an *n*th-order reaction would occur at 0% conversion. In addition, an induction period is associated with no apparent heat release prior to the initiation and acceleration of the decomposiiton reaction. Figure 2 demonstrates the autocatalytic characteristics of cumene hydroperoxide thermostated at 75°C and defines the terminology that is useful for describing autocatalytic behaviors in an isothermal environment. Data summarized from analysis composed to previous are presented in Table 2. Onset temperature of cumene hydroperoxide was detected as low as 75°C using the thermal activity monitor; however, the heat of decomposition was about 85% compared to that determined by DSC dynamic scanning. A possible explanation for the differences in apparent heat of reaction is that the cumene hydroperoxide molecules at a lower temperature possessed inherently lower kinetic energy for overcoming the reaction activating energy that could result in a different reaction branching ratio, less decomposition, and, subsequently, less heat of decomposition.

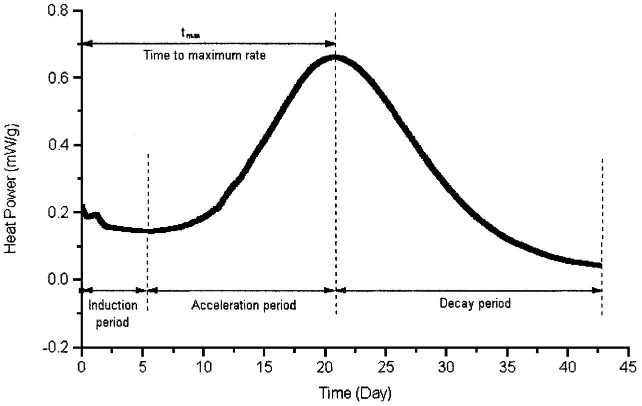

Figure 2. Autocatalytic behaviors of 80 wt. % cumene hydroperoxide thermostated at 75°C.

Conclusions

This study demonstrates the application of the isothermal microcalorimeter for investigating the autocatalytic exothermic decomposition of cumene hydroperoxide. Identification of the autocatalytic decomposition of organic peroxides is crucial, since these materials can generate catalysts that could lead to a delayed thermal runaway or an explosion in an isothermal environment. Isothermal microcalorimetry is a promising approach for investigating other organic peroxides where the thermal decomposition mechanisms and kinetics could be unique. Data from autocatalytic thermograms can be used to assess the thermal runaway or reactive hazards potential of organic peroxides and to determine useful parameters such as exothermic onset temperature, isothermal TMR_{ad} (compared to adiabatic time to maximum rate) detected by adiabatic calorimetry and ΔT_{ad} (adiabatic temperature rise) evaluated from ΔH (heat of decomposition).

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