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THERMAL DECOMPOSITION KINETICS OF CUMENE HYDROPEROXIDE

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The thermal decomposition and runaway reaction of cumene hydroperoxide (CHP) in cumene were studied by thermal analysis and by using the VSP-II adiabatic calorimeter. Decomposition kinetics were determined in various CHP concentrations in cumene. The reaction order of 20wt%, 35wt%, 50wt%, 65wt%, and 80wt% was determined to be 0.5, and the Arrhenius parameters were measured as Ea (kJmol⁻¹) = 122.0 ± 3.0 and ln A (min⁻¹ M^{1/2}) = 30.0 ± 1.2. This new determination of the reaction order as equal to one half implies the same mechanism of decomposition regardless of CHP concentration. Chromatography and IR spectroscopy was combined with calorimetry data to determine the thermal decomposition kinetics. The preliminary rate determining step was considered to be the decomposition of CHP by dimer association. A reaction mechanism for CHP thermal decomposition is proposed.

Keywords: cumene hydroperoxide; thermal decomposition kinetics.

INTRODUCTION

Most organic peroxides can be used to initiate free-radical polymerization. In fact, this application accounts for about 90% of the total consumption in Taiwan. However, many thermal runaway or explosion incidents have been caused by the decomposition of organic peroxides due to their thermal instabilities or reactive incompatibilities (Table 1)¹. Hydroperoxides (such as hydrogen peroxide and cumene hydroperoxide) are extremely sensitive or reactive to acids, metal ions and impurities.

The process of organic hydroperoxide decomposition in a variety of solvents is usually more complicated compared with other organic peroxides catagories (e.g. dialkyl peroxides or ketone peroxides). A previous report² indicated that thermal decomposition of cumene hydroperoxide (CHP) was dependent upon the CHP concentration. Based on the accelerating rate calorimeter (ARC) test and the isothermal and dynamic differential scanning calorimeter (DSC) tests, the reaction order of 35 wt% CHP decomposition was determined to be 0.5. The Arrhenius parameters were measured² to be *Ea* (kJmol⁻¹) = 120.6 ± 3.0 and ln A (min⁻¹M^{1/2}) = 30.2 ± 1.3 .

The aim of this research was to continue our work to verify the thermal decomposition kinetics and the mechanism of CHP in non-isothermal and isothermal conditions. Both DSC and VSP-II (Vent Sizing Package II) techniques were used for thermal analysis to obtain thermal kinetics data. Identification of the intermolecular and intramolecular hydrogen-bonded association of CHP was carried out using infrared (IR) spectroscopy. The decomposition kinetics of CHP, affected by its associated complex, have been confirmed by incorporating the thermokinetic data, IR spectroscopic and chromatographic methods. A reaction mechanism for CHP thermal decomposition was proposed from the identification of some distinguishing decomposition products by the chromatographic method.

EXPERIMENT

Sample

Eighty wt% CHP purchased directly from the supplier was measured to determine both density and concentration, then stored in a 4°C environment. Cumene was used as the dilution solvent in preparing various CHP samples.

DSC (Differential Scanning Calorimeter)

The dynamic screening and isothermal experiments were performed on a Mettler TA4000 system coupled with a DSC25 measuring cell³. The system was connected to an IBM PC computer in which data were evaluated and stored. Disposable high pressure crucibles (ME-26732) were used for acquiring thermograms and isothermal traces. Standard aluminum crucibles were used for heat capacity (C_P) measurements. The average heat capacity ($Jg^{-1}K^{-1}$) of various solutions of cumene hydroperoxide of 80%, 35%, 20% and 15% were determined to be 2.219, 2.217, 2.154 and 2.074, respectively. The measuring method was used to check the heat capacity temperature function of aluminum oxide (α -Al₂O₃ single crystal) with the data provided by the National Bureau of Standards (NBS). The scanning rate chosen for the temperature programmed ramp was chosen to be 4K min⁻¹.

VSP (Vent Sizing Package)

A PC controlled adiabatic calorimeter system, the Vent Sizing Package II (VSPII) manufactured by FAI⁴, was used

Table 1. Thermal explosion accidents caused by peroxide in Taiwan.

Date	Chemicals	Injuries	Fatalities	Hazard	Cause
1979 7.13	MEKP ^a	49	33	Explosion (Storage)	Thermal decomposition
1981 4.21	CHP^b	3	1	Explosion (Condensation)	Thermal decomposition
1984 2.18	MEKP ^a	55	5	Explosion (Reactor)	Thermal decomposition
1986 5.02	CHP^b	0	0	Explosion (Reactor)	Thermal decomposition
1987 9.05	H_2O_2	20	0	Explosion (Storage)	Incompatibility
1988 7.25	TBHP ^c	19	0	Explosion (Storage)	Cooling failure
1989 3.14	Organic Peroxide	0	0	Fire (Tank)	Cooling failure
1989 8.04	Organic Peroxide	0	0	Fire (Storage)	Cooling failure
1989 9.01	MEKP ^a	5	7	Explosion (Storage)	Thermal decomposition
1996 10.07	MEKP ^a	47	10	Explosion (Storage)	Thermal decomposition

^a Methyl Ethyl Ketone Peroxide, MEKP

^b Cumene Hydroperoxide, CHP

^c Tert-Butyl Hydroperoxide, TBHP

to measure the thermokinetic and thermal hazard data such as temperature and pressure trace in relation to time. The low heat capacity of the cell ensures that essentially all the reaction heat released remains within the test sample. Thermokinetics and pressure behaviour in the small test cell (112 ml) can therefore be extrapolated directly to the process scale due to the low thermal inertia of about 1.05 to 1.2. Three types of cells for closed testing, top venting or bottom dumping are available. Detailed information on the performance of the VSP calorimeter can be found in the literature ^{5,6}. Basic design data for emergency relief systems can be acquired from the VSPII calorimeter and related DIERS methodology. The two-phase flow pattern, such as churn-turbulent or homogeneous equilibrium flow, can be determined directly from top venting experiments using the VSP II.

IR (Infrared Spectra)

Infrared spectra were measured with a Bornem MB FT-IR instrument using a solution cell made of KBr. The spectrum range from 400 cm⁻¹ to 4000 cm⁻¹ was scanned to seek the characteristic bands or fingerprints associated with molecular vibrations, bendings and interactions.

Chromatographic studies

The decomposition products were identified by HPLC using a UV-970 detector employing $C18 \,\mu m$

column. The eluting solvent was a mixture of acetonitrile and water (3:7) at a flow rate of $1.3 \,\mathrm{ml\,min^{-1}}$. The detection was carried out at a wavelength of 254 nm. A gas chromatography (HP5890 series II plus) linked with a Mass Dectector (HP5972) were also used to monitor the decomposition products using a RTX-502.2 column ($60.0m \times 0.32 \mathrm{mmID} \times 1.8 \,\mu\mathrm{m}$). The carrier gas was helium at pressure around 10.0 psig. The injection temperature was set at 225°C.

Table 2. Heat of decomposition and initial exothermic temperature of cumene hydroperoxide.

	a	METTLER DSC 25			
	Scan rate (°C min ⁻¹)	T_0 (°C)	ΔH	I (Jg ⁻¹)	$\Delta H (\mathrm{Jg}^{-1})$
35%CHP	10	110	626.7	1790 (100%)	1874 (100%)
	4	95	618.6	1767 (100%)	(JRIIS)
	2	80	618.7	1768 (100%)	
	1	80	640.0	1828 (100%)	
50%CHP	2	90	883.0	1766 (100%)	1874 (100%) (JRIIS)
65%CHP	2	90	1172.6	1804 (100%)	1874 (100%)
	2	90	1503.2	1879 (100%)	(JRÌIS)
80%CHP	4	100	1424.8	1781 (100%)	1874 (100%)
	4	100	1417.6	1772 (100%)	(JRIIS)

CHP: Cumene Hydroperoxide

 T_0 : thermal decomposition initial exothermic temperature

 ΔH : heat of decomposition

JRIIS: Japan Research Reports of Research Institute of Industrial Safety⁷

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Figure 1. The heat flow versus temperature of dynamic thermal decomposition of different CHP concentrations.

RESULTS AND DISCUSSION Thermal Analysis

The onset temperature and heat of decomposition of CHP can be easily acquired by using DSC programmed scanning. Figure 1 shows the typical temperature and heat flow curves for the thermal decomposition of 50wt%, 65wt% and 80wt% CHP/cumene solution. The thermal decomposition hazards of CHP with different concentrations can be characterized using a non-isothermal method. The peaks on the thermograms indicate that the higher CHP concentrations will result in potential hazard in the case of thermal decomposition. Thermal analysis data are listed in Table 2. The onset temperature was determined to be 80°C. The heat of decomposition was measured to be (1810 ± 50) J per gram of CHP and this was in good agreement with another study⁷. However, the onset temperature was determined to be about 150°C by using a higher scanning rate of 20 $Kmin^{-1}$ in the annual reports of JRIIS⁷.

Hydrogen-Bonded Association

In the IR spectra, a series of concentrated solutions of CHP (5wt%~ 80wt%) in cumene showed the hydrogenbonded effect of the —O-H stretching vibration. Two distinguishable peaks were observed in Figure 2 and listed in Table 3. The $u_{0.H}$ bond centered at 3430.56cm⁻¹ (band 1) was due presumably to free CHP with a bridge between the —O-O-H group and the π -electrons of the aromatic ring. This result suggests that the formation of associates by intramolecular hydrogen bonding and the $u_{0.H}$ is not influenced by CHP concentration.

However, another absorbance (band 2) occurred at 3489 cm^{-1} and shifted to 3502 cm^{-1} with increasing concentration, which was assigned to be the -O-H stretching mode. This was due to the higher association and increased gradually with increasing concentration^{8,9}. The absorption peak of -O-H stretching was originally at 3300 cm^{-1} without any perturbations of intermolecular or intramolecular hydrogen bonding. The shifted phenomena of the absorption peak was due to the intermolecular hydrogen bounding formed between the -O-H functional group(s) and the oxygen atom(s) of

$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\$

Wavenumber(cm⁻¹)

Figure 2. Infrared absorption spectrum of cumene hydroperoxide in cumene.

the cyclic dimers.

$$2\text{ROOH} \rightleftharpoons [\text{ROOH}]_2 \tag{1.1}$$

$$R - O - R$$
(1.2)

where $R = (C_6H_5)C(CH_3)_2$).

Evidently one can expect that the formation of associates can retard the decomposition of organic hydroperoxides by affecting the reaction order of the decomposition pathway as well as the activation energy. The formation of a dimeric structure indicates that the rate-determinating step depends strongly on the concentration of dimer associates. It has been found that the dimeric associate of the hydroperoxide was the most stable structure and could be investigated using IR spectroscopy even at $75^{\circ}{}^{9}$.

Decomposition Kinetics

Isothermal method

Previous work in this laboratory has shown the correlation of runaway behaviour with respect to CHP concentration. It was found that the reaction order of

 Table 3. Infrared absorption bands of cumene hydroperoxide in cumene (22°C).

	Band centre 1 cm ⁻¹ (transmittance)	Band centre 2 cm ⁻¹ (transmittance)
5%	3430.56 (0.829)	3502.21 (0.550)
10%	3430.56 (0.586)	3501.37 (0.329)
20%	3430.56 (0.257)	3497.37 (0.214)
40%	3430.56 (0.057)	3489.23 (0.043)
80%	3430.56(0)	3461.52 (0)

35wt% CHP decomposition was 0.5. The dynamic method described above does not lead to a full understanding of the complex decomposition mechanism. On the other hand, isothermal analysis does eliminate the thermal lag effect and maintains good thermal equilibrium using a *n*th-order model.

The rate equation for various CHP concentrations can be written as

$$-d[CHP]/dt = k[CHP]^n$$
(2)

Equation (2) can be integrated and becomes

$$[CHP]^{1-n} = (n-1)kt + [(CHP)_0]^{1-n}$$
(3)

The isothermal tests were conducted at 140° C with a series of different concentrations, or at fixed concentration with different temperatures. As shown in Table 4, the reaction order was determined to be a constant value of 0.5 in spite of differences in temperature or concentration.

Non-isothermal method

Interpretation of IR and thermal analysis data from dynamic and isothermal DSC verifies the formation of association complexes in various CHP/cumene mixtures. The non-isothermal approach was performed by using an adiabatic calorimeter VSPII. A model for CHP thermal decomposition kinetics was proposed in the following equations.

$$dQ/dt = k[CHP]^{1/2} \Delta HV\rho$$
(4)

$$dT/dt = k \frac{(T_f - T_0)^{1/2}}{([CHP]_0)^{1/2}} [T_f - T]^{1/2}$$
(5)

The experimental measurements of self-heating rate and temperature behaviour in 15wt% CHP were in good agreement with the theoretical calculation data. The self-accelerating temperature to time curve was recorded in Figure 3. Figure 4 shows that the experimental data on self-heating rate were in fact bounded quite closely to the proposed model with a reaction order of 0.5. VSPII experiment data of CHP 15wt% are summarized in Table 5.

Table 4. The reaction order determined from DSC isothermal experiments.

	20%	35%	50%	65%	80%
120℃	_	_	_	_	0.51
130°C		_		0.48	0.50
140°C	0.49	_	0.50	0.49	0.52
150°C	0.52	0.50	0.50	0.50	0.51
160°C	0.52	—	0.47	0.52	0.50



Figure 3. The time versus temperature for thermal decomposition of CHP 15wt%.



Figure 4. The self-heating rate versus temperature for thermal decomposition of CHP $15wt^{\circ}$.

The Chromatographic Data of the CHP Decomposition

The detection of decomposition products of CHP at various temperatures ($130^{\circ}C \cdot 140^{\circ}C \cdot 150^{\circ}C$) proves the presence of acetone, α -methylstyrene, and acetonphenol. But 2-phenyl, 2-propanol and phenol, not detected by gas

Table 5. VSP II experiment data of CHP15%.

Items	Values
CHP wt%	15%
CHP weight (g)	8.47
Cumene weight (g)	48.0
Total sample weight (g)	56.47
Total sample volume (ml)	64.03
Can weight (g)	43.0
Can volume (ml)	112
Ζ	1.19
T_0 (°C)	100
T_f (°C)	206.2
T_{Cf} (°C)	210.9
$(dT/dt)_{max}$ (°C min ⁻¹)	2.80
$(dT/dt)_{cmax}$ (°C min ⁻¹)	4.80
$C_p (Jg^{-1} K^{-1})$	2.074
ΔH (J/g CHP100%)	1810
$\ln A (\min^{-1} M^{1/2})$	29.71
$Ea (J \text{ mol}^{-1})$	125000
$[CHP]_0$ (M)	0.87

Table 6. Analyses of CHP composition products from gas chromatography.

Temperature Product	130℃	140℃	150℃
Acetone	100.000^{a}	4.426	79.679
α -Methylstyrene	46.600	100.000^{a}	69.190
Acetophenone	5.082	18.954	100.000 ^a

^{*a*} The highest intensity as base peak.

 Table 7. Analysis of CHP decomposition products ratios by HPLC diluted

 1000 times.

Temperature			
Product	130°C	140°C	150°C
Acetone	1.306	1.178	1.344
Acetophenone	1.366	4.420	8.422
Phenol	100.000^{a}	100.000^{a}	100.000^{a}
2-Phenyl, 2-propanol	1.302	1.965	2.354

^{*a*} The highest intensity as base peak.

 Table 8. Analysis of CHP decomposition products ratio by HPLC diluted 100 times.

Temperature Product	130℃	140℃	150℃
Acetone	12.598	12.686	10.115
Acetophenone	10.057	7.125	3.050
Phenol	100.000^{a}	100.000^{a}	100.000^{a}
2-Phenyl, 2-propanol	5.166	16.847	8.823

^{*a*} The highest intensity as base peak

chromatography, were clearly identified by HPLC. Interestingly, α -methylstyrene, not detected by HPLC, was shown using gas chromatography. These final products can be regarded as direct evidence for proposing the decomposition mechanism of CHP. The ratios of decomposition products at various temperatures are shown in Table 6, Table 7 and Table 8.

Mechanism of Thermal Decomposition

Evidence about the major products of CHP decomposition as verified by GC and HPLC chromatography are associated with kinetic data, an overall rate law of 0.5 order, and the mechanism of CHP thermal decomposition are proposed in this study. A free radical reaction scheme for the thermal decomposition of CHP in cumene is as follows:

$$\begin{aligned} & 2C_{6}H_{5}C(CH_{3})_{2}OOH \xrightarrow{k_{1}}_{k_{-1}} [C_{5}H_{3}C(CH_{3})_{2}OOH]_{2} \\ & \text{Fast equilibrium, } k_{1} \gg k_{-1} \\ & C_{6}H_{5}C(CH_{3})_{2}OOH \xrightarrow{k_{2}} C_{6}H_{5}C(CH_{3})_{2}O \cdot + OH \text{ slow} \\ & C_{6}H_{5}C(CH_{3})_{2}O \cdot \xrightarrow{k_{3}} C_{6}H_{5}COCH_{3} + OH_{3} \\ & C_{6}H_{5}C(CH_{3})_{2}H + OH_{3} \xrightarrow{k_{4}} CH_{4} + C_{6}H_{5}C(CH_{3})_{2} \\ & C_{6}H_{5}C(CH_{3})_{2}H + OH \xrightarrow{k_{5}} H_{2}O + C_{6}H_{5}C(CH_{3})_{2} \\ & C_{6}H_{5}C(CH_{3})_{2}O \cdot + C_{6}H_{5}C(CH_{3})_{2}H \xrightarrow{k_{6}} \\ & C_{6}H_{5}C(CH_{3})_{2}O + C_{6}H_{5}C(CH_{3})_{2}H \\ & C_{6}H_{5}C(CH_{3})_{2}O + C_{6}H_{5}C(CH_{3})_{2}C \\ & C_{6}H_{5}C(CH_{3})_{2$$

$$C_{6}H_{5}C(CH_{3})_{2}O' + OH \xrightarrow{k_{7}} C_{6}H_{5}OH + CH_{3}CCH_{3}$$

$$\bigcup_{O}$$

$$C_{6}H_{5}C(CH_{3})_{2}' + OH \xrightarrow{k_{8}} C_{6}H_{5}CCH_{3} = CH_{2} + H_{2}O$$

$$2C_{6}H_{5}C(CH_{3})_{2}' \xrightarrow{k_{9}} [C_{6}H_{5}C(CH_{3})_{2}]_{2} \qquad (6)$$

The overall rate law can be derived from the reaction scheme and rate-determining step.

$$R = \frac{-d[C_6H_5C(CH_3)_2OOH]}{dt} = k_2[C_5H_5C(CH_3)_2OOH]$$
(7)

and

$$[C_{6}H_{5}C(CH_{3})_{2}OOH] = \left[\frac{k_{-1}}{k_{1}}(C_{6}H_{5}C(CH_{3})_{2}OOH)^{2}\right]^{1/2}$$
(8)

According to the evidence of intermolecular hydrogenbonding from IR spectra and studies of the literature^{8,9}, most of the CHP molecules are associated into the extremely stable dimers via a –O-H----O bond. The initial and decomposition concentrations of CHP were simplified to be

$$\frac{1}{2} \left[C_6 H_5 C(CH_3)_2 OOH \right]_{t=0} = \left[(C_6 H_5 C(CH_3)_2 OOH_2 \right]_{t=0}$$
(9)

and

$$\frac{1}{2} \left[C_6 H_5 C(CH_3)_2 OOH \right]_{(t)} = \left[C_6 H_5 C(CH_3)_2 OOH \right]_{(t)}$$
(10)

Therefore, the overall rate law for CHP in thermal decomposition can be represented in the following equation.

$$R = \frac{k_2 k_{-1}^{1/2}}{k_1^{1/2}} [C_6 H_5 C(CH_3)_2 OOH)_2]^{1/2}$$

= $\frac{k_2 k_{-1}^{1/2}}{k_1^{1/2}} \left[\frac{1}{2} (C_6 H_5 C(CH_3)_2 OOH)_{(l)} \right]^{1/2}$
= $k [C_6 H_5 C(CH_3)_2 OOH)_{(l)}]^{1/2}$ (11)

where k is the overall rate constant.

The heat of decomposition is proportional to isolated CHP molecules or dimeric forms. The thermokinetics and adiabatic temperature behaviour are still the same with this model.

CONCLUSION

The thermal decomposition of organic alkylperoxides has been studied and is well represented by simple first-order kinetics. However, special attention has been paid to the organic hydroperoxide category. The kinetics and mechanism of the decomposition of hydroperoxides are of great importance with regard to the association of intermolecular and intramolecular hydrogen-bondings. A systematic approach to verify the decomposition pathway is addressed. The application of IR, chromatography, non-isothermal and isothermal DSC and VSPII methodologies are promising techniques for generating the data for the study of decomposition kinetics. The rate-determining step is the decomposition of the associated peroxides into radicals. The

V

overall rate constant is independent of the solvent present. The reaction order of CHP/cumene decomposition was determined to be 0.5.

APPENDIX: Derivation of equation (5)

For an adiabatic environment,

$$-\Delta H \left(\frac{-\mathrm{d}[\mathrm{CHP}]}{\mathrm{d}t}\right) V = mC_P \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) \tag{A.1}$$

$$-\frac{\mathrm{d}[\mathrm{CHP}]}{\mathrm{d}t} = \frac{mC_P}{\Delta HV} \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) \tag{A.2}$$

$$-\int_{[CHP]_0}^{[CHP]} d[CHP] = -\frac{mC_P}{\Delta HV} \int_{T_0}^T dT$$
(A.3)

$$[CHP] = [CHP]_0 + \frac{mC_P}{\Delta HV}(T - T_0)$$
(A.4)

For a 0.5 order reaction of CHP decomposition

$$\frac{-\mathrm{d}[\mathrm{CHP}]}{\mathrm{d}T} = k[\mathrm{CHP}]^{1/2} \tag{A.5}$$

Combining equation (A.2), (A.4) and (A.5)

$$-\frac{mC_P}{\Delta HV} \left(\frac{dT}{dt}\right) = k[CHP]^{1/2} = k[[CHP]_0 + \frac{mCP}{\Delta HV}(T - T_0)]^{1/2}$$
(A.6)

The CHP concentration can be related to the change of temperature.

$$-\Delta H = \frac{mC_P}{[\text{CHP}]_0 V} (T_f - T_0)$$
(A.7)

Equations (A.7) and (A.6) are combined and give

NOMENCLATURE

C_P	specific heat capacity, Jg ⁻¹ K ⁻¹
Κ	rate constant, sec ⁻¹ M ¹⁻ⁿ
n	reaction order
dQ/dt	heat generation rate, W
ΔH	heat of reation, KJ mol ⁻¹

volume of reactant, 1
density of reactant, gl ⁻¹
mass of reactant, g
temperature, K
initial exothermic temperature, K
final temperature, K
calc. final temperature, K
time, min
the max self-heating rate, °C min ⁻¹

volume of reactant 1

 $(dT/dt)_{max}$ the max self-heating rate, $C \min(dT/dt)_{cmax}$ the calc. max self-heating rate, $C \min^{-1}$

dT/dt self-heating rate, $^{\circ}C \min^{-1}$

R rate of reaction, Msec⁻¹

Z thermal inertia

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