Thermal Hazard Analysis of Methyl Ethyl Ketone Peroxide

Ron-Hsin Chang, Chi-Min Shu and Po-Yin Yeh

Process Safety and Disaster Prevention Laboratory,
Department of Environmental and Safety Engineering,
National Yunlin University of Science and Technology,
Touliu, Yunlin, Taiwan 640, R.O.C.

Mei-Ling Shyu
Department of Electrical and Computer Engineering, University of Miami,
Coral Gables, FL 33124-0640, U.S.A

Shu-Ching Chen
Distributed Multimedia Information System Laboratory, School of Computer Science,
Florida International University, Miami, FL 33199, U.S.A.

Abstract

In the past forty years in Japan and Taiwan, many thermal explosions have been caused by methyl ethyl ketone peroxide (MEKPO) under the influence of external fire and others. Thermograms of commercialized MEKPO dimers were first screened by Differential Scanning Calorimetry (DSC) to determine the heat of decomposition and exothermic onset temperature. Thermal runaway phenomena were then thoroughly investigated by Vent Sizing Package2 (VSP2). Data of thermokinetics and hazard behaviors were used for hazard analysis of MEKPO thermal explosions.

The onset temperatures of MEKPO monomer, which was prepared by the reaction of methyl ethyl ketone (MEK) and H_2O_2, were determined to be at about 40 ^oC, showing extremely dangerous while operating in hot ambient conditions, which is the first finding in literature. The novel finding shows that two peaks on the thermograms that indicate the MEKPO thermal runaway is a complicated reaction mechanism,

requiring further study for detailed thermal hazard investigation in the future.

Instead of normal one reaction peak from the adiabatic calorimeter, two exothermic peaks on the DSC thermograms is another novel finding among literatures. It was found that the reaction order of 1st peak of MEKPO dimer decomposition by isothermal analysis was 1. The Arrhenius parameters were calculated to be E_a (kcal mol^{-1}) = 27.0 and lnA (s^{-1}) = 29, with reproducible confirmation. The reaction order of the 2nd peak of MEKPO dimer decomposition was 0.3 by DSC, showing the Arrhenius parameters of E_a (kcal mol^{-1}) = 27.5 and lnA (s^{-1}) = 23. By VSP2 the Arrhenius parameters were determined as lnA (s^{-1}) = 20.7, E_a (kcal mol^{-1}) = 20.3, and n = 1, respectively. Preventative measures can be established by these basic parameters so that the pro-active disaster prevention program can be practically achieved.

Keywords: methyl ethyl ketone peroxide, Differential Scanning Calorimetry, Vent Sizing Package2 (VSP2), thermal runaway, Arrhenius parameters.

Introduction

Many thermal explosions caused by methyl ethyl ketone peroxide (MEKPO) under the influence of external fire have occurred in Japan and Taiwan in the past forty years, as shown in Tables 1 and 2 (Duh, 1998). In Taiwan, one of the worst accidents was the Yung-Hsin plant explosion occurred in 1996. The initial fire was due to out of control of oxidation reaction in process site, which was then spread to the tank yard. The fire-induced thermal explosion killed 10 and injured 47 people during the fire fighting. In Tokyo, 3,600 kg (8,000 lb) of MEKPO exploded under the influence of a fire in 1964, killing 19 and wounding 114 people, along with the damage of 1.25 U.S. million dollars (AIChE, 1995).

MEKPO, which is a common name of peroxides produced by reacting methyl ethyl ketone (MEK) with hydrogen peroxide (H_2O_2), is widely used in industry as a radical catalyst source for initiating and cross-linking polymerization. In practice, commercial MEKPO is not a single compound but with isomers. Theoretically, seven different types of MEKPO might be co-existed (Milas, 1959), but only monomer and dimer forms have prevailed (OSHA, 1989). Due to the complex molecular structure, some of them possess higher potential of reactive hazard and thermal sensitivity than others. In NFPA 43B, the property of MEKPO has been recognized as class Ⅲ and Ⅳ shown in Table 3 (NFPA 43B, 1999). To comply with the U.S. Department of Transportation (DOT) shipping regulations, the MEKPO should be diluted to weight percent concentration of 60 wt % or less with dimethylphthalate (DMP) as shown in Table 4 (DOT, 1990). The largest quantity of a commercial package was limited to be 5 gallons by NFPA 43B.

The decomposition of MEKPO is extremely complicated because of its readical-induced reaction mechanism. Objectively, this study was to investigate the

safety margins for processing and a acquire proper knowledge to identify the hazard for operating MEKPO and validate thermal hazard characteristics of MEKPO dimer under runaway conditions. Therefore, in this study, Differential Scanning Calorimetry (DSC) and Vent Sizing Package2 (VSP2) were used, along with thermal analysis techniques to measure thermokinetics data, specifically for runaway assessment. Thermograms of commercialized MEKPO were first screened by DSC to determine the heat of decomposition and exothermic onset temperature. Thermal runaway phenomena were then thoroughly investigated under adiabatic environment by VSP2. Data of thermokinetics and hazard potentials were used for hazard analysis of MEKPO thermal explosion. The resulted temperature-time profile and self-heat rate, based on the thermal runaway theory of Townsend and Tou, were manipulated to determine parameters in the exothermic decomposition reaction kinetics (Barton, 1997; Townsend, 1980).

Experiment

Samples. 32wt % MEKPO was purchased directly from the Fluka Co., then stored in a 4 ^{o}C refrigerator. As mentioned above, DMP was used as the dilutent solvent in preparing various MEKPO samples. On the other hand, the MEKPO monomer was synthesized by reacting MEK with H_2O_2. Two typical forms of MEKPO are shown in Figure 1 (OSHA, 1989).

DSC (Differential Scanning Calorimetry). Temperature-programmed screening and isothermal experiments were performed on a Mettler TA8000 system coupled with a DSC821^{e} measuring cell that can withstand relatively high pressure to approximately 100 bar. Star^{e} software was used for obtaining thermograms and isothermal traces (Mettler, 1998). For better thermal equilibrium purposes, the scanning rate chosen for the temperature-programmed ramp was 4 ^{o}Cmin^{-1} (Hou, 2001).

VSP2 (Vent Sizing Package2). A PC-controlled adiabatic calorimeter system, the Vent Sizing Package2 (VSP2) manufactured by Fauske Associates, Inc. (FAI, 1996), was utilized to measure the thermokinetic and thermal hazard data such as temperature and pressure traces with respect 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 behaviors 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 (Wang, 2001). The worst credible case can be also simulated under adiabatic, cooling failure or external fire conditions, to name a few.

Results and Discussion

Thermal Analysis by DSC. In general, a DSC-programmed scanning can readily acquire the onset temperature and heat of decomposition of MEKPO dimer. Figure 2 shows the typical temperature and heat flow curves for the thermal decomposition of 4 wt %, 8 wt %, 16 wt % and 32 wt % MEKPO/DMP solution, respectively. The thermal decomposition hazards of MEKPO with different concentrations can be characterized by using a non-isothermal method. The heat of MEKPO thermal decomposition with different concentrations was measured, resulting in good agreement among these tests. According to the results, the onset temperatures were determined at about 110 ^{o}C. The heat of decomposition was measured to be (3,300±250) J per gram of MEKPO dimer (100 wt %). Data of thermal analyses are listed in Table 5. Results of physical data including heat of decomposition, initially exothermic onset temperature, heat flow, and curves of thermograms are suitable for exhibiting the strength of reactivity as well as thermal hazards of MEKPO dimer. The novel finding shows that two peaks on the thermograms indicate that the MEKPO dimer thermal runaway is a complicated reaction mechanism, requiring further study for detailed thermal hazard investigation in the future (Shu, 2001).

Apparently, the dynamic method described above does not direct to a full understanding of the complex decomposition mechanism of MEKPO. Contrasting to the dynamic method, isothermal analysis does eliminate the thermal lag effect and maintain better thermal equilibrium than using n-th order model. The isothermal tests were conducted between 100 ^{o}C and 130 ^{o}C with a series of different concentrations followed by dynamic test with scanning rate in 4 ^{o}Cmin^{-1} to determine reaction order of MEKPO, as shown in Table 6.

The onset temperatures of MEKPO monomer prepared from reaction of MEK

and H_2O_2 were determined to be at about 40 ^oC which is the first finding in literature. It will be more hazardous and unstable because of the lower temperature exothermic phenomenon shown in Figure 3, in which three sample weights of 2.2 mg, 2.4 mg and 2.5 mg illustrate the very close and consistent results. The monomer type has illustrated higher heat flow at lower temperature, higher heat of decomposition than the dimer one, as shown in Figure 4. Owing to the different molecular structure compared to the dimer, onset temperature of MEKPO monomer measured in DSC is even as low as 40 ^oC, demonstrated an extremely high degree of thermal hazard while being handled under hot ambient conditions.

Thermal Analysis byVSP2. The characteristic curves of time versus temperature of MEKPO dimer are recorded in Figure 5. The main reason, which shows the maximum temperature of 45 ml MEKPO dimer exceeds the 60 ml, may be ascribed to the fact that the depth of thermocouple is located at the interface between the liquid phase and gas phase of the test cell. In view of the limitation of VSP2 with higher concentration of MEKPO dimer, VSP2 experimental data of 10 wt % MEKPO dimer are summarized in Table 7. The onset temperature of 10 wt % MEKPO was chosen to be the exothermic temperature which reaches the sensitivity of the VSP2 calorimeter. Defining the temperature with self-heat rate of 0.1 ℃ min^{-1} as the initial temperature, the onset temperature of 10 wt % MEKPO is 88℃ with the thermal inertia (Φ) of 1.16. The only one peak appeared in VSP2 was due to the first exothermal peak as heat being accumulated to exceed the onset temperature of second exothermal peak ($T_{01} + \Delta T_{AD} > T_{02}$). Figure 6 indicates the self-heat rate vs. temperature where the maximum self-heat rate is 21.8 $^oCmin^{-1}$. The major decomposition products of MEKPO dimer are carbon dioxide, water, acetic acid, formic acid and methyl ethyl ketone (AKZO, 1996).

The maximum temperature of 10 wt % MEKPO dimer during the adiabatic runaway was determined to be 238 ^{o}C, which explained the MEKPO is a highly hazardous material. The released gas products were 2.87×10^{-2} moles per gram MEKPO, which can be correlated to the severity of thermal explosion caused by heat source, such as an external fire.

Kinetics Analysis by DSC. Isothermal analysis compared with Borchardt and Daniel method were used in kinetics analysis by DSC calorimetry (Borchardt, 1956). Based on the isothermal measurement results, the Arrhenius plot of lnk versus 1/T with different temperatures is a straight line, providing the activation energy for MEKPO dimer decomposition. The reaction order of 1st peak of MEKPO dimer decomposition by isothermal analysis was determined to be 1st order. The Arrhenius parameters were calculated to be E_a (kcal mol^{-1}) = 27.0 and lnA (s^{-1}) = 29. In addition, the second peak was checked with standard decomposition reaction of 20 wt % di-tert-butyl peroxide (DTBP) in toluene, then applied to MEKPO dimer studies. The Arrhenius parameters of DTBP with first order decomposition were determined to be E_a (kJmon^{-1}) = 157 and lnA (s^{-1}) = 36.0 in excellent accordance with previous studies (Duh, 1997; Shaw, 1968). The reaction order of the 2nd peak of MEKPO decomposition was 0.3 by DSC, indicating the Arrhenius parameters of E_a (kcal mol^{-1}) = 27.5 and lnA (s^{-1}) = 23, as shown in Table 8.

Kinetics Analysis by VSP2. Adiabatic decomposition kinetics of 10 wt % MEKPO can be deduced from the relationship between temperature and time or via the self-heat rate (Townsend, 1980). A pseudo zero-order rate constant (k^*) for n-th order exothermic decomposition reaction can be calculated from the observed self-heat rate at specific temperature (T).

$$k^* = C_0^{n-1} k = \frac{m_T}{(\frac{T_f - T}{\Delta T_{AD}})^n \Delta T_{AD} C_0^{n-1}} \quad (1)$$

This can be related to the Arrhenius equation (Eq (2)):

$$\ln k^* = \ln C_0^{n-1} A - \frac{E_a}{R}(\frac{1}{T}) \quad (2)$$

As expected from experimental data, the plot of $\ln k^*$ versus 1/T is a straight line which is assumed that the order of reaction is chosen correctly in Figure 7. The Arrhenius parameters were determined as lnA (s^{-1}) = 20.7, E_a (kcal mol^{-1}) = 20.3, and n = 1, respectively. Based on the methodology of Design Institute for Emergency Relief system (DIERS) of AIChE, these values are very helpful while designing the pressure relief system specifically under runaway reaction during processing, transportation, and storage periods.

Table 9 summarizes the overall Arrhenius parameters measured with the VSP2 and by the other studies (Lee, 1969; Stull, 1977; ITRI, 1994).

Conclusions

This study demonstrates that the application of calorimetry techniques for investigating the exothermic decomposition of MEKPO is a promising way of generating the data necessary for reaction hazard analysis which can, in turn, identify the rule in safer shipping and handling of MEKPO reaction synthesis.

MEKPO is a common name used in the chemical industries, however the characteristics of thermal decomposition behaviors were quite different. From this study, it concludes that monomer type MEKPO is the most hazardous one among the compound series owing to the lower decomposition temperature. High heat-releasing rate is ascribed to the kinetics during decomposition. Severe consequence caused by MEKPO thermal explosion could be explained by the features of large quantity of heat of decomposition, non-condensed gas products and specific rate constant.

The experimental data from thermal calorimetery can provide fundamental safety characteristics and can be utilized to pro-actively prevent the occurrence of thermal runaway reactions.

Nomenclature

ΔH	heat of reaction, kJ mol^{-1}
ΔH_d	heat of decomposition, kJ mol^{-1}
ΔH_1	heat of decomposition for first peck, kJ mol^{-1}
ΔH_2	heat of decomposition for second peck, kJ mol^{-1}
$(dP/dt)_{maj}$	maximum pressure rise rate, psi min^{-1}
$(dT/dt)_{max}$	maximum self-heat rate, $^oCmin^{-1}$
dT/dt	self-heat rate, $^oCmin^{-1}$
$(dT/dt)_0$	self-heat rate at onset temperature, $^oCmin^{-1}$
E_a	apparent activation energy, $kJmole^{-1}$
k	rate constant, $sec^{-1}M^{1-n}$
lnA	fractional factor, s^{-1}
m	mass of reactant, g
n	reaction order, dimensionless
P_{max}	maximum pressure, psig
R	rate of reaction, $Msec^{-1}$
T	temperature, ^oC
t	time, min
T_0	initial exothermic temperature, ^oC
T_{01}	first peak of initial exothermic temperature, ^oC
T_{02}	second peak of initial exothermic temperature, ^oC
T_f	final temperature, ^oC
T_{max}	maximum temperature, ^oC
TMR	time to maximum rate, min
V	volume of reactant, ml

ρ	density of reactant, gl^{-1}

Acknowledgements

The authors wish to thank the Ministry of Education of R. O. C. for instrument support through the program of the Education Improvement for Civil Disaster Prevention.

Literature Cited

(1)Duh, Y. S.; Kao, C. S.; Hwang, H. H.; Lee, W. L. Thermal Decomposition Kinetics of Cumene Hydroperoxide. *Trans. Inst. Chem. Eng*, **1998**, 76B, 271.

(2)Safe Storage and Handling of Reactive Materials. Published by Center for Chemical Process Safety of the AIChE, New York, USA, **1995,** 226.

(3)Milas, N.A.; Golubovic, A. Studies in Organic Peroxides. XXV. Preparation, Separation and Identification of Peroxides Derived from Methyl Ethyl Ketone and Hydrogen Peroxide. *J. Am. Chem. Soc.*, **1959**, 81, 5824.

(4)Methyl Ethyl Ketone Peroxide -Organic Method # 77; OSHA **1989**, 1.

(5)Code for the Storage of Organic Peroxide Formulations, NFPA 43B; National Fire Protection Association, Quincy, MA, USA, **1999**.

(6)Federal Register, Department of Transportation, Part Ⅱ, USA, **1990**, 55.

(7)Barton, J.; Rogers, R. Chemical Reaction Hazards-A Guide. Institution of Chemical Engineers, 2nd ed., Davis Building, UK, **1997**, 42.

(8)Townsend, D. I.; Tou, J. C. Thermal Hazard Evaluation by An Accelerating Rate Calorimeter. *Thermochim. Acta,* **1980**, 37, 1.

(9)STAR^{e} Software with Solaris Operating System, Operating Instructions; Mettler Toledo, **1998**.

(10)VSP2 Manual and Methodology; Fauske & Associates, Inc., USA, **1996**.

(11)Wang, Y. W.; Shu, C. M.; Duh, Y. S.; Kao, C. S. Thermal Runaway Hazards of Cumene Hydroperoxide with Contaminants. *Ind. Eng. Chem. Res.* **2001**, 4, 1125.

(12)Akzo Nobel Chemicals, Inc., Curing Agents for Thermoset Resins. **1996**, 1.

(13)Borchardt, H. J.; Daniels, F. The Application of Differential Analysis to the Study of Reaction Kinetics. *J. Am. Chem. Soc*. **1956**, 79, 41.

(14)Duh, Y. S.; Kao, C. S.; Lee, C.; Yu, S. W. Runaway Hazard Assessment of Cumene Hyproperoxide form the Cumene Oxidation Process. *Trans. Inst. Chem. Eng.* **1997**, 75B, 73.

(15)Shaw, D. H.; Pritchard, H. A. Thermal Dcomposition of Di-tert-butyl Peroxide at High Pressure. *Can. J. Chem.* **1968**, 46, 2721.

(16)Lee, P. R. Safe Storage and Transportation of Some Potentially Hazardous Materials. *J. Appl. Chem.* **1969**, 19, 345.

(17)Stull, D. R. Fundamentals of Fire and Explosion. *AIChE Monograph Series*, **1977**, 73, 21.

(18)Shu, C.M.; Yeh, P. Y. Thermal Hazard Analysis of Methyl Ethyl Ketone Peroxide, Ispra (VA), Italy, **2001**.

(19)Hou, H. Y.; Shu, C.M.; Duh, Y. S. Exothermic Decomposition of Cumene Hydroperoxide at Low Temperature Conditions. AIChEJ (R & D Note). (Accepted)

(20) 陳美玲，Duh, Y. S.，柏雅玲，有機過氧化物之熱危害評估，ITRI, **1994**.

Figure Captions

Figure 1. Two typical forms of MEKPO (OSHA, 1989).

Figure 2. DSC thermograms of MEKPO dimer with concentrations of 4 wt %, 8 wt %, 16 wt % and 32 wt %, respectively.

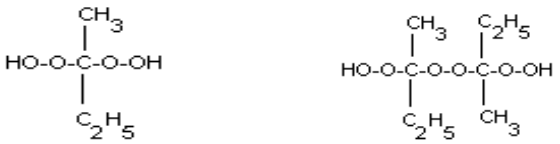
Figure 3. Three DCS thermograms of MEK reacted with H_2O_2 for 2.2 mg, 2.4 mg, and 2.5 mg sample weights, respectively.

Figure 4. DCS thermograms of MEK reacted with H_2O_2, MEKPO dimer and H_2O_2, respectively.

Figure 5. The temperature versus time curve for the decomposition reaction of 10 wt % MEKPO dimer with 30 ml, 45 ml and 60 ml, respectively.

Figure 6. The self-heat rate versus temperature curves for the decomposition reaction of 10 wt % MEKPO dimer with 30 ml, 45 ml and 60 ml, respectively.

Figure 7. The pseudo rate constant versus temperature of thermal decomposition reaction of 10 wt % MEKPO dimer.



Monomer Dimer

Figure 1. Two typical forms of MEKPO (OSHA, 1989).

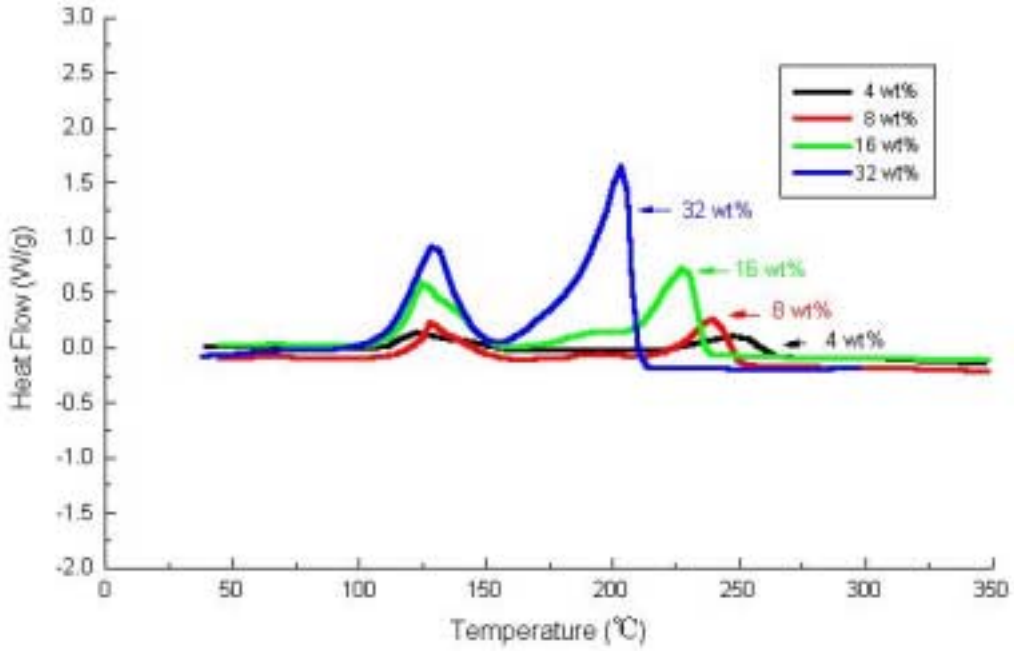


Figure 2. DSC thermograms of MEKPO dimer with concentrations of 4 wt %, 8 wt %, 16 wt % and 32 wt %, respectively.

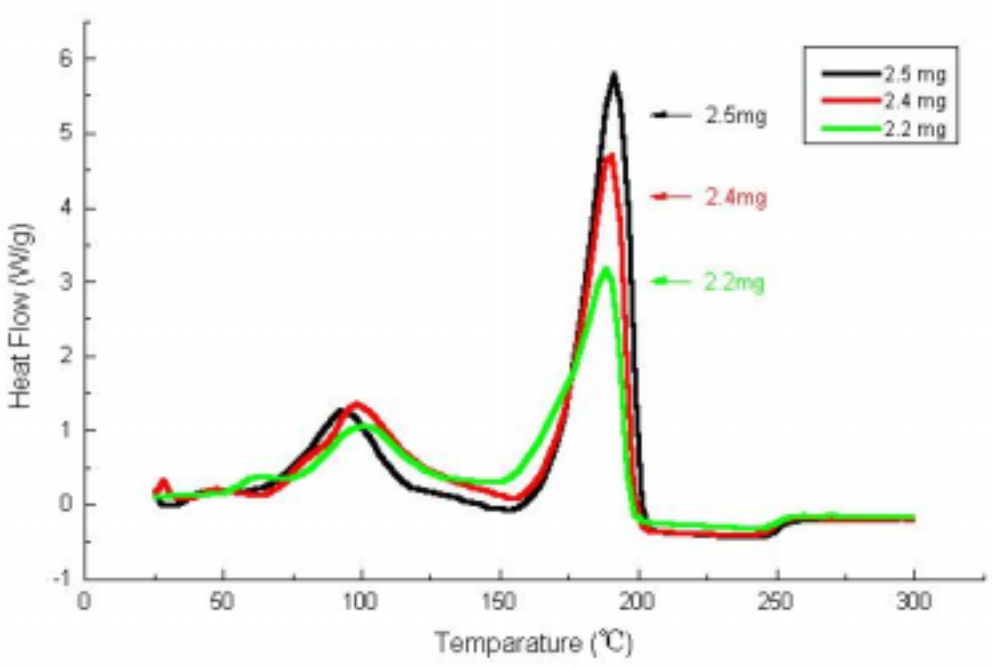


Figure 3. Three DCS thermograms of MEK reacted with H_2O_2 for 2.2 mg, 2.4 mg, and 2.5 mg sample weights, respectively.

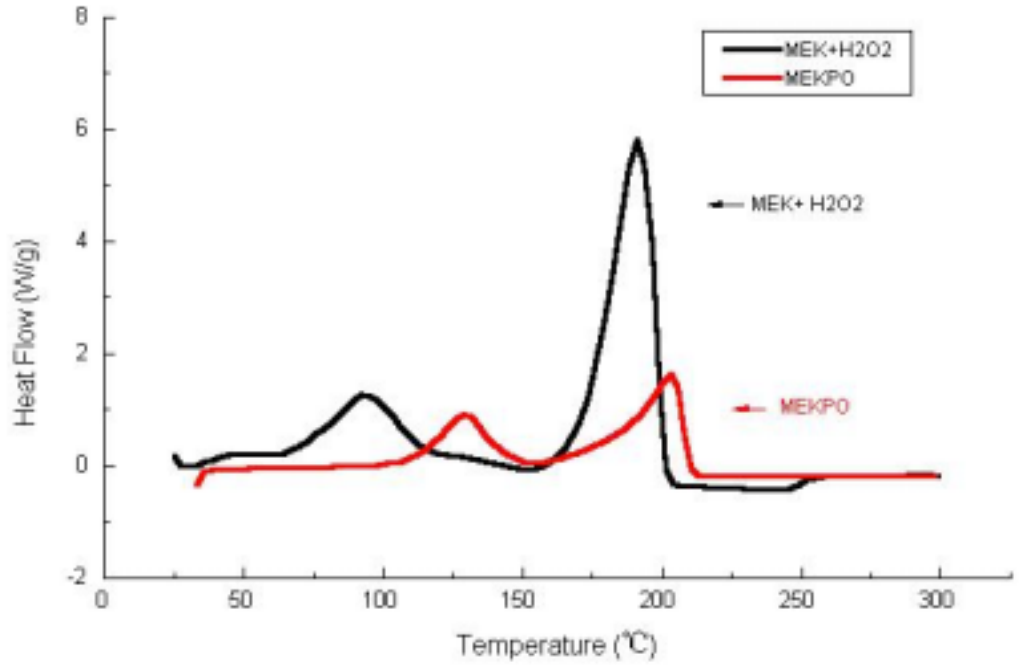


Figure 4. DCS thermograms of MEK reacted with H_2O_2, MEKPO dimer and H_2O_2, respectively.

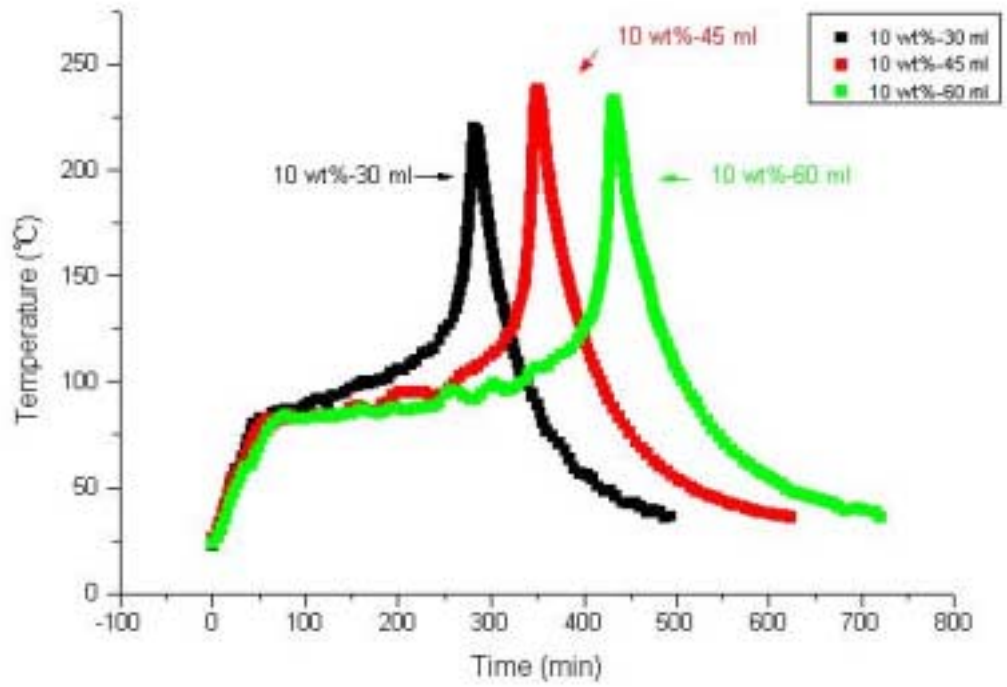


Figure 5. The temperature versus time curve for the decomposition reaction of 10 wt % MEKPO dimer with 30 ml, 45 ml and 60 ml, respectively.

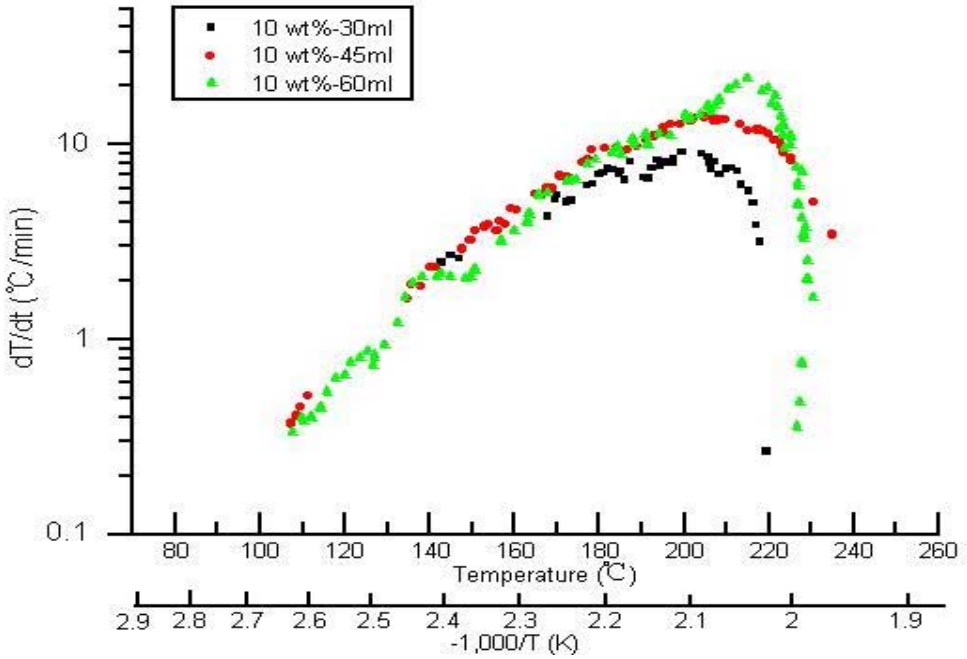


Figure 6. The self-heat rate versus temperature curves for the decomposition reaction of 10 wt % MEKPO dimer with 30 ml, 45 ml and 60 ml, respectively.

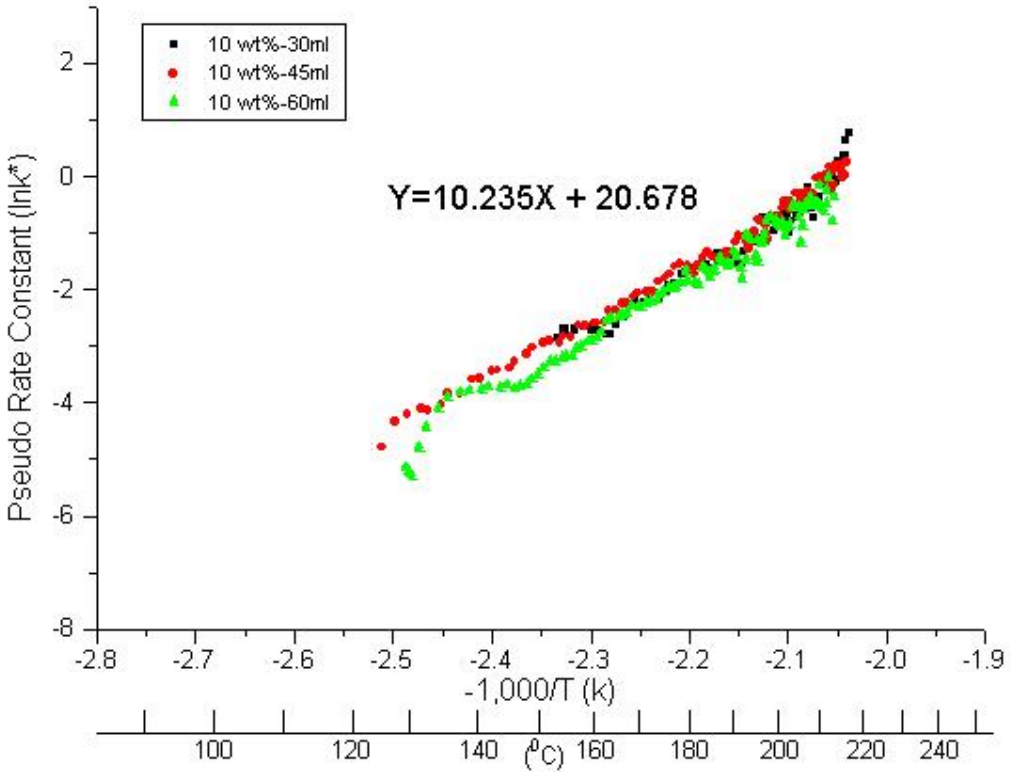


Figure 7. The pseudo rate constant versus temperature of thermal decomposition reaction of 10 wt % MEKPO dimer.

Table Captions

Table 1. Thermal Explosion Incidents Caused by Thermal Decomposition of MEKPO in Taiwan Since 1979 (Duh, 1998)

Table 2. Thermal Explosion Incidents Caused by Thermal Decomposition of MEKPO in Japan Since 1953

Table 3. NFPA 43B Classification of Organic Peroxides (MEKPO) for Storage and Shipping (NFPA 43B, 1999)

Table 4. Package Requirements and Other Provisions for Organic Peroxide Regulated by DOT Regulation Code (DOT, 1990)

Table 5. The Onset Temperature and Heat of Decomposition of MEKPO Dimer by DSC

Table 6. Isothermal and Dynamic Data on Thermal Decomposition of MEKPO dimer by DSC Dimer

Table 7. Data of VSP2 Test Results for 10 wt % MEKPO Dimer

Table 8. Thermal Analysis of MEKPO Dimer by DSC

Table 9. Various Parameters Derived from Thermal Decomposition of MEKPO (Lee, 1969; Stull, 1977; ITRI, 1994)

Table 1. Thermal Explosion Incidents Caused by Thermal Decomposition of MEKPO in Taiwan Since 1979 (Duh, 1998)

Date	Location	Injuries	Fatalities	Hazard
1979.07.13	Taipei	49	33	Explosion (Storage)
1984.02.18	Taoyuan	55	5	Explosion (Reactor)
1989.09.01	Taoyuan	5	7	Explosion (Tank)
1996.10.07	Taoyuan	47	10	Explosion (Tank)

Table 2. Thermal Explosion Incidents Caused by Thermal Decomposition of MEKPO in Japan Since 1953

Date	Location	Weight	Injuries	Fatalities
1953.06.29	Tokyo	3 kg	0	3
1953	Hyougo	0.1 kg	0	1
1958	Tokyo	NA[(1)]	0	0
1958.08	Aichi	0.1 kg	1	0
1958	Nara	8 kg	0	0
1958	Aichi	16 kg	0	0
1958	Osaka	NA	0	0
1958	Osaka	NA	0	0
1960	Tokyo	NA	0	0
1962	Tokyo	0.5 kg	0	0
1964.07.14	Tokyo	3,600 kg (8,000 lb)	114	19
1964	Tokyo	NA	0	0
1965	Tokyo	NA	0	0
1978.06	Kanagawa	5 kg	0	0

(1) NA: Not Applicable

Table 3. NFPA 43B Classification of Organic Peroxides (MEKPO) for Storage and Shipping (NFPA 43B, 1999)

Definition		Concentration (wt %)	Diluent Solvent	Maximum Container Size
Class Ⅲ	Methyl Ethyl Ketone Peroxide	9 AO	DMP	5 gal
Class Ⅳ	Methyl Ethyl Ketone Peroxide	5.5 AO	Alcohols & Ketones	5 gal
	Methyl Ethyl Ketone Peroxide	9.0 AO	DMP Water & Glycols	5 gal

AO: Active Oxygen

DMP: Dimethyl Phthalate

Table 4. Package Requirements and Other Provisions for Organic Peroxide Regulated by DOT Regulation Code (DOT, 1990)

Technical Name	ID Number	Concentration (Mass %)	Diluent (Mass %)			Water (Mass %)	Packing Method	Temperature (^{o}C)		Remarks
			A	B	I	NA		Control	Emergency	
Methyl Ethyl Ketone Peroxide	UN3101	≦52	≧48			NA	OP5A	NA		AO＜9 %
Methyl Ethyl Ketone Peroxide	UN3105	≦45	≧55			NA	OP7A	NA		AO＜9 %
Methyl Ethyl Ketone Peroxide	UN3107	≦40	≧60			NA	OP8A	NA		AO＜9 %

A:A is an organic liquid that does not detrimentally affect the thermal stability or increase the hazard of the organic peroxide and with a boiling point not less than 150 ^{o}C at atmospheric pressure. Type A diluents may be used for desensitizing all organic peroxide.

B: The boiling point of a type B diluent must be at least 50 ^{o}C above the control temperature of the organic peroxide.

I: An inert solid is a solid that does not detrimentally affect the thermal stability or increase the hazard of the organic peroxide.

UN3101: Organic peroxide type B, liquid

UN3105: Organic peroxide type D, liquid

UN3107: Organic peroxide type E, liquid

OP5A, OP7A and OP8A: Packages for liquid organic peroxides

AO: Active Oxygen

NA: Not Applicable

Table 5. The Onset Temperature and Heat of Decomposition of MEKPO Dimer by DSC

		Peak 1		Peak 2		Peak 1+Peak 2
Concentration (wt %)	Scanning Rate ($^{o}Cmin^{-1}$)	T_{o1} (^{o}C)	$\triangle H_1$ ($J\ g^{-1}$)	T_{o2} (^{o}C)	$\triangle H_2$ ($J\ g^{-1}$)	$\triangle H_1+\triangle H_2$ ($J\ g^{-1}$)
32	4	107.72	324.70	171.09	706.70	3,223.1 (100 wt %)
16	4	116.87	214.21	201.73	337.40	3,425.8 (100 wt %)
8	4	121.56	95.86	218.92	149.68	3,069.3 (100 wt %)
4	4	122.12	49.42	219.12	91.44	3,521.5 (100 wt %)

Table 6. Isothermal and Dynamic Data on Thermal Decomposition of MEKPO dimer by DSC Dimer

	Peak 1		Peak 2		Peak 1+Peak 2
Concentration (wt %)	Isothermal Temperature (^{o}C)	$\triangle H_1$ ($J\ g^{-1}$)	Dynamic Scanning Rate ($^{o}C\ min^{-1}$)	$\triangle H_2$ ($J\ g^{-1}$)	$\triangle H_1+\triangle H_2$ ($J\ g^{-1}$)
32	130	316.23	4	704.02	3,188.28 (100 wt %)
16	130	159.05	4	338.38	3,108.93 (100 wt %)
8	130	62.10	4	191.64	3,171.75 (100 wt %)
4	130	54.12	4	73.46	3,189.50 (100 wt %)

Table 7. Data of VSP2 Test Results for 10 wt % MEKPO Dimer

Sample (ml)	Φ	T_o （^oC）	P_{max} (psig)	T_{max} (^oC)	$(dP/dt)_{max}$ (psig min^{-1})	$(dT/dt)_{max}$ (^oC min^{-1})	$(dT/dt)_0$ (^oC min^{-1})	Number of Gas Moles Decomposed
30	1.32	96	226.84	219.88	30.62	10.79	0.1	9.12×10^{-3}
45	1.21	93	334.15	238.22	55.86	15.12	0.1	1.62×10^{-2}
60	1.16	88	414.3	232.89	80.27	21.8	0.1	2.87×10^{-2}

Table 8. Thermal Analysis of MEKPO Dimer by DSC

	Isothermal	Peak 1				Peak 2			
Concentration (wt %)	Temperature (^oC)	lnk (s^{-1})	E_a (kcal mol^{-1})	lnA (s^{-1})	n	Concentration (wt %)	E_a (kcal mol^{-1})	lnA (s^{-1})	n
32	100	-7.71	27.0	29	1	32	27.5	23.0	0.3
	110	-6.8				16			
	120	-5.8				8			
	130	-5.07				4			

Table 9. Various Parameters Derived from Thermal Decomposition of MEKPO (Lee, 1969; Stull, 1977; ITRI, 1994)

Reference /Apparatus	Substance (Concentration)	T_o (℃)	Peak Number	n	E_a (kcalmol^{-1})	lnA (s^{-1})	$\triangle H_d$ (kcalmol^{-1})
Lee (1969) /NA	MEKPO (NA)	NA	NA	NA	28.7	27.4	NA
Stull (1977) /NA	MEKPO (NA)	NA	NA	NA	NA	NA	-52.20
ITRI (1994) /ARC	MEKPO (NA)	65	1	NA	NA	NA	-29.51
This work /VSP2	MEKPO dimer (10 wt %)	88	1	1	20.3	20.7	-17.56
This work /DSC	MEKPO dimer (32 wt %)	$110^{(1)}+170^{(2)}$	2	$1^{(1)}+0.3^{(2)}$	$27.0^{(1)}+27.5^{(2)}$	$29^{(1)}+23^{(2)}$	-51.20

(1): 1st peak

(2): 2nd peak

NA: Not Applicable