Adiabatic runaway studies for methyl ethyl ketone peroxide with inorganic acids by vent sizing package 2

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Abstract−Methyl ethyl ketone peroxide (MEKPO) is an unstable material that is classified as an explosive substance. We evaluated MEKPO 10 mass% under mixing with three inorganic acids (6 N HNO_3, 6 N H_3PO_4, and 6 N H_2SO_4) by adiabatic system of vent sizing package 2 (VSP2). Results from evaluation and testing indicated that these three inorganic acids could increase the degree of hazard while combined with pure MEKPO. Therefore, information on the hazards and phenomena of runaway reaction should be provided in order to lessen the degree of hazard.

Key words: Methyl Ethyl Ketone Peroxide, Inorganic Acids, Vent Sizing Package 2 (VSP2), Runaway Reaction, Degree of Hazard

INTRODUCTION

Kinetic parameters of methyl ethyl ketone peroxide (MEKPO) by curve fitting method often include apparent activation energy (E_a), frequency factor (A), and heat of reaction (ΔH). In the last four decades, MEKPO has also been developed as a radical source for initiation as a cross-linker during polymerization. Over the years, it has caused many serious accidents in Asia [1]. If the temperature is not well controlled, the system may become unstable and eventually encounter a runaway reaction, potentially leading to various types of accidents [2-4]. Therefore, serious attention should be paid to a chemical reactor that contains an unstable reactive chemical such as hydrogen peroxide [5-7]. In a systematic study of MEKPO 10 mass% tested by vent sizing package 2 (VSP2), we elucidated the kinetic parameters of mixing three inorganic acids with MEKPO 10 mass%.

Many investigators [8-11] have employed related devices and methods to evaluate the kinetic model of an n-order or autocatalytic reaction, demonstrating the innate characteristics of hazardous substances such as lauroyl peroxide [12] and nitrobenzene [13]. To precisely choose a kinetic model for evaluating runaway reactions, two factors associated with the curve fitting method must be taken into account for evaluating kinetic parameters. First, the experimental data should fit properly into the curve fitting system. The performance of a kinetic model of n-order, autocatalytic, or other complex reaction provided us with valuable information on evaluating the design of MEKPO 10 mass% with inorganic acids. Second, selecting a correct or reasonable kinetic model is important for calculating the kinetic parameters.

Herein we report our new findings that MEKPO 10 mass% can

cause critical reactions when it is mixed with three inorganic acids. Our results indicate that the exothermic onset temperature (T_o), ΔH, and E_a can be used to evaluate the degree of hazard during a manufacturing process.

EXPERIMENTAL SETUP AND CURVE FITTING

MEKPO 31 mass% was obtained from the Fluka Co., and then stored in a refrigerator at 4 °C. Dimethyl phthalate (DMP) was used as the diluent solvent in preparing the concentrations of MEKPO 10 mass%. De-ionized water (H_2O) was used as the diluent in preparing H_2SO_4 (6 N), HNO_3 (6 N), and H_3PO_4 (6 N). DMP 99 mass% was added into MEKPO 31 mass% for preparing MEKPO 10 mass%. The reaction mixture was then stirred at room temperature in the dark for 30 minutes. H_2SO_4 (6 N, 5 mL), HNO_3 (6 N, 5 mL), or H_3PO_4 (6 N, 5 mL) were individually added into MEKPO (10 mass%, 50 mL) for testing each different type of mixture condition.

VSP2 was used to measure experimental data such as temperature and pressure. The heat-wait-search (H-W-S) mode for detecting the self-heating rate was adopted for VSP2. If the self-heating rate is larger than 0.1 °C min^{-1}, the H-W-S and main heater will be immediately terminated for measuring the original phenomenon of self-exothermicity. All reactions were carried out in a test cell (112 mL). The thermal inertia of the test cell was reported to be between 1.05 and 1.2 [14].

After finishing the VSP2 test, we output the experimental data (time, temperature, and pressure) into this curve fitting system to calculate and optimize the kinetic parameters. There are various types of kinetic models; we employed an n-order or autocatalytic reaction to fit the experimental data for precisely acquiring kinetic parameters. The kinetic models used by this study are shown as follows [15].

A formal model can represent complex multi-stage reactions that

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include several independent, parallel, and consecutive stages.
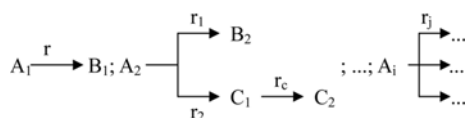
The corresponding mathematical model is represented by the system of ordinary differential equations, Eqs. (1)-(3):

$$r_i = \frac{d\alpha_i}{dt} = \sum_j r_{ij}; \quad r_{ij} = k_{ij}(T) f_j(\alpha_i) \tag{1}$$

$$k_i(T) = k_{0i} e^{-E_{ai}/RT} \tag{2}$$

$$\frac{dQ_i}{dt} = \sum_j Q_{ij}^{\infty} r_{ij} \tag{3}$$

where r_i and α_i denote the reaction rate and conversion degree of the corresponding reactant of i-th independent reaction; r_{ij} is the reaction rate of the j-th stage; f_j is the kinetic function describing the dependency of reaction rate on the conversion; dQ_i/dt is the overall rate of heat generation of i-th independent reaction; r_{ij} and Q_{ij} denote reaction rate and heat effect of the j-th stage. In addition, $k_i(T)$ obeys the Arrhenius temperature dependence of rate constant, and k_{0i} and E_{ai} represent the frequency factor and activation energy of the i-th independent reaction. R is the gas constant (=8.314 J mol^{-1} K^{-1}). Examples of the formal model are illustrated in the following: Simple single-stage reaction A→B

$$\frac{d\alpha}{dt} = k_0 e^{-E_a/RT} f(\alpha); \tag{4}$$

$$f(\alpha) = \begin{cases} (1-\alpha)^n\text{-N-order model} \\ (1-\alpha)^{n_1}(\alpha^{n_2}+z)\text{-Autocatalytic model} \\ (1-\alpha)(-\ln(1-\alpha))^n\text{-Avrami-Erofeev model} \end{cases}$$

Runaway includes two consecutive stages A→B→C

$$\frac{d\alpha}{dt} = k_{01} e^{-E_1/RT}(1-\alpha)^{n_1} \tag{5}$$

$$\frac{d\gamma}{dt} = k_{02} e^{-E_2/RT}(\alpha-\gamma)^{n_2} \tag{6}$$

where α and γ are conversions of the reactant A and product C, respectively.

There are two parallel reactions:

A→B+…----Initiation stage
A+B→2B+…----Autocatalytic reaction

These are very useful models of full autocatalysis:

$$\frac{d\alpha}{dt} = r_1(\alpha) + r_2(\alpha) \tag{7}$$

$$r_1(\alpha) = k_1(T)(1-\alpha)^{n_1} \tag{8}$$

$$r_2(\alpha) = k_2(T)\alpha^{n_2}(1-\alpha)^{n_3} \tag{9}$$

The above-mentioned equations can be used for establishing the thermal stability of MEKPO and determining the reaction hazard. All of the experimental data and kinetics evaluation results were obtained by employing the ADPro and ForK software developed by CISP Ltd. [16]. By using this system, we also can evaluate the safety parameter of time-to-maximum rate (TMR).

RESULTS AND DISCUSSION

VSP2 was used to obtain the experimental data, and then the kinetic parameters were calculated by curve fitting; the results are displayed in Tables 1 and 2. There were two types of kinetic schemes

Table 1. Calculated thermokinetic parameters derived from the VSP2 of MEKPO 10 mass% and with HNO$_3$ (6 N)

MEKPO and contaminant	Φ	Kinetic scheme	T_0 [°C]	E_a [kJ mol^{-1}]	n_1	n_2	A [M^{1-n} sec^{-1}]	z	ΔH [J g^{-1}]
MEKPO 10 mass%, 50 mL (first stage)	1.19	n-Order		107.58	0.94	NA	26.05	NA	43.15
MEKPO 10 mass%, 50 mL (second stage)		Autocatalysis	102	36.06	2.94	1.51	7.74	0.005	46.19
MEKPO 10 mass%, 50 mL+HNO$_3$ (6 N), 5 mL (first stage)	1.19	n-Order		79.33	0.70	NA	20.03	NA	61.99
MEKPO 10 mass%, 50 mL+HNO$_3$ (6 N), 5 mL (second stage)		Autocatalysis	60	93.82	2.09	0.38	22.78	0.05	59.38

--- Calculated values based on experimental data from VSP 2 tests.
--- Curve fitting values.
NA: Not applicable.

Table 2. Calculated thermokinetic parameters derived from the VSP2 of MEKPO 10 mass% mixed with H$_3$PO$_4$ (6 N) and H$_2$SO$_4$ (6 N)

MEKPO and contaminant	Φ	Kinetic scheme	T_0 [°C]	E_a [kJ mol^{-1}]	n	A [M^{1-n} sec^{-1}]	ΔH [J g^{-1}]
MEKPO 10 mass%, 50 mL+H$_3$PO$_4$ (6 N), 5 mL	1.19	n-Order	91	71.06	0.52	14.61	70.41
MEKPO 10 mass%, 50 mL+H$_2$SO$_4$ (6 N), 5 mL	1.19	n-Order	53	76.61	0.79	19.04	93.00

--- Calculated values based on experimental data from VSP 2 tests.
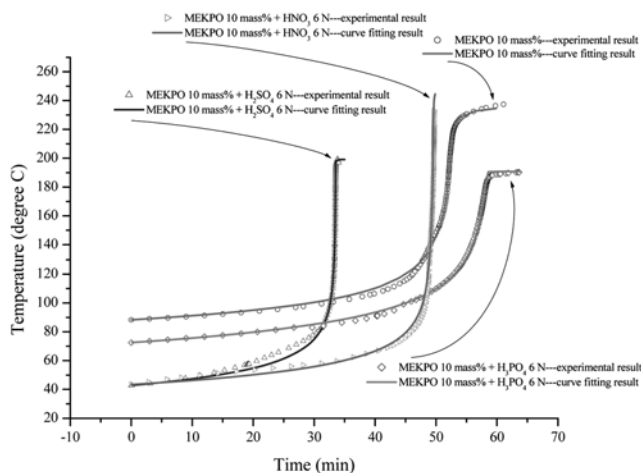**--- Curve fitting values.**

Fig. 1. Simulated temperature vs. time by VSP 2 experiments for MEKPO 10 mass% with HNO₃ 6 N, H₃PO₄ 6 N, and H₂SO₄ 6 N, respectively.

that could be selected for curve fitting a pure condition or complex one with the addition of inorganic acids, such as HNO_3, H_3PO_4, or H_2SO_4. Most of the mixing conditions provided strong evidence that mixture-reaction conditions had been induced to create a more unsafe situation than the pure one.

Our results in Tables 1 and 2 show the calculated thermokinetic parameters derived from the VSP2 of the pure and mixing conditions. From Fig. 1, when MEKPO was mixed with inorganic acids, T_o was induced to occur earlier in comparison with the pure condition. The reaction of MEKPO 10 mass% mixed with HNO_3, H_3PO_4, and H_2SO_4 lowered T_o to 60, 91, and 53, respectively, as compared with the pure MEKPO of 102. Therefore, the degree of hazard had been increased during the period of mixture. This is because the unstable O-O structure of MEKPO is very sensitive to inorganic acids, which can enhance the ability of decomposition reactions and heat of reaction.

The thermal decomposition of MEKPO generally gives some free radicals, but the detailed mechanism is not known yet. Here, Fig. 2 shows the mechanism of the initiation stage for the decomposition of MEKPO alone [17-21]. However, in the presence of a strong mineral acid the activation energy of the initiation stage decreases. Although the acidity of phosphoric acid is not as strong as sulfuric acid, the H^+ ion can still accelerate the decomposition rate of MEKPO and break the unstable structure of O-O. From our experiment, however, the phosphoric acid delayed the H_3PO_4 catalyst reaction at the second stage. In Fig. 3, the phosphorus species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) will abstract OH free radicals to become more stable intermediates because phosphorus species act as

$$PO_4^{3-} \ + \ \cdot OH \longrightarrow products \quad (Black \ and \ Hayon)[24]$$

$$HPO_4^{2-} \ + \ \cdot OH \longrightarrow products \quad (Maruthamuthu \ and \ Neta)[25]$$

$$H_2PO_4^- \ + \ \cdot OH \longrightarrow products \quad (Maruthamuthu \ and \ Neta)[25]$$

$$H_3PO_4 \ + \ \cdot OH \longrightarrow products \quad (Jiang, \ P.\text{-}Y., \ et \ al)[26]$$
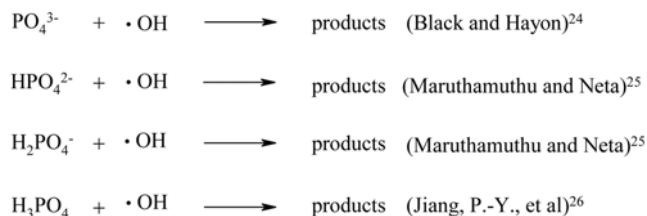
Fig. 3. Scavenging of hydroxy radicals by phosphate system a=ref 24, b=ref 25, c=ref 26.

an OH radical scavenger [22-26]. Therefore, the heat of reaction only increased from 43.15 J g⁻¹ (pure MEKPO) to 70.41 J g⁻¹, as compared to 93.00 J g⁻¹ of the sulfuric acid. As H_3PO_4 was employed during producing the MEKPO, we only evaluated its effect on MEKPO via reaction mechanism.

On the other hand, E_a was calculated to confirm the ability of decomposition reactions. If the value of E_a decreases in a complex reaction, a decomposition reaction could be more easily triggered under lower exothermic conditions. The reaction of MEKPO 10 mass% mixed with HNO_3, H_3PO_4, and H_2SO_4 lowered the value of E_a to 79.33, 71.06, and 76.61 kJ mol⁻¹, respectively, as compared to the pure MEKPO of 107.58 kJ mol⁻¹. Due to the unstable feature of MEKPO, especially mixed with inorganic acids, adding an inhibitor to increase E_a should be considered while dealing with complex or unstable reactions during transportation or storage.

Curve fitting results from our systematic studies clearly indicated that TMR under mixing conditions was decreased, as seen in Fig. 4 and Table 3. For example, when MEKPO 10 mass% was mixed with HNO_3 and H_2SO_4, the TMR could be reached at 1.6 and 3.2 hrs, respectively, at 27 °C, which is much earlier compared to 749 hours for pure MEKPO. Therefore, a cooling system must be employed for controlling the temperature while mixing conditions have been induced.
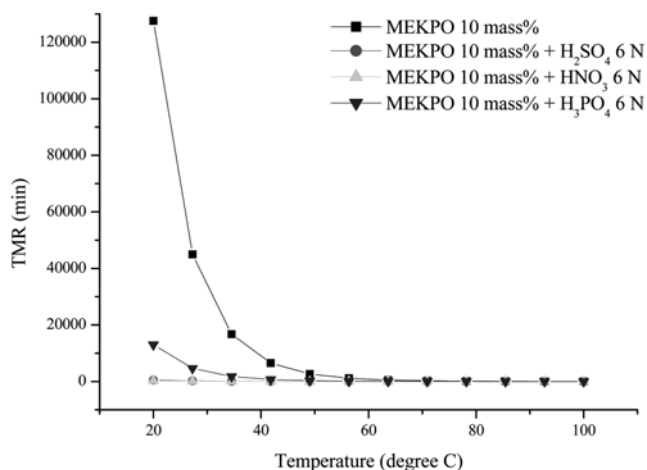
CONCLUSIONS

Fig. 2. Proposed initiation stage of decomposition mechanisms of pure MEKPO.

Fig. 4. Simulated TMR vs. temperature by VSP 2 experiments for MEKPO 10 mass% with HNO₃ 6 N, H₃PO₄ 6 N, and H₂SO₄ 6 N, respectively.

Table 3. Calculated TMR derived from curve fitting method of MEKPO 10 mass% and with HNO$_3$ (6 N), H$_3$PO$_4$ (6 N), and H$_2$SO$_4$ (6 N)

MEKPO 10 mass%		MEKPO 10 mass%+ HNO$_3$ 6 N		MEKPO 10 mass%+ H$_3$PO$_4$ 6 N		MEKPO 10 mass%+ H$_2$SO$_4$ 6 N	
Temperature [°C]	Time [hour]	Temperature [°C]	Time [hour]	Temperature [°C]	Time [hour]	Temperature [°C]	Time [hour]
20.00	2125.71	20.00	4.68	20.00	216.75	20.00	7.90
27.27	749.17	27.27	1.64	27.27	77.49	27.27	3.24
34.55	278.02	34.55	0.60	34.55	29.20	34.55	1.39
41.82	108.24	41.82	0.23	41.82	11.53	41.82	0.62
49.09	44.07	49.09	0.09	49.09	4.78	49.09	0.29
56.36	18.72	56.36	0.04	56.36	2.06	56.36	0.14
63.64	8.26	63.64	0.02	63.64	0.92	63.64	0.07
70.91	3.78	70.91	0.0078	70.91	0.43	70.91	0.04
78.18	1.79	78.18	0.0037	78.18	0.21	78.18	0.02
85.45	0.879	85.45	0.0018	85.45	0.10	85.45	0.01
92.73	0.44	92.73	0.0008	92.73	0.05	92.73	0.005
100.00	0.23	100.00	0.0005	100.00	0.027	100.00	0.003

New mixing conditions of MEKPO 10 mass% mixed with HNO$_3$, H$_3$PO$_4$, and H$_2$SO$_4$ were studied by experimental and curve fitting methods. The runaway reaction was explored to a greater extent. MEKPO was found to be unstable for its structure of O-O, especially while mixed with inorganic acids; as such, it is highly exothermic and induces a runaway reaction under a loss of control situation or T$_o$ occurs earlier during mixing conditions. Such an unstable structure of O-O in MEKPO content may have played an important role in runaway reactions. By utilizing the above-mentioned methods, we elucidated the phenomena and characteristics of runaway reactions for MEKPO. This safety information could alleviate the degree of hazard during storage or transfer processes.

ACKNOWLEDGMENTS

REFERENCES

1. Y. S. Duh, C. S. Kao, H. H. Hwang and W. L. Lee, *Trans. Inst. Chem. Eng.*, **76B**, 271 (1998).
2. G. S. Chuang, A. C. Chao and H. Y. Li, *Korean J. Chem. Eng.*, **21**, 963 (2004).
3. K. S. Kim and J. W. Ko, *Korean J. Chem. Eng.*, **22**, 26 (2005).
4. Y. W. Nam and K. S. Park, *Korean J. Chem. Eng.*, **21**, 370 (2004).
5. A. Amornchai, P. Kittisupakorn and M. A. Hussain, *Korean J. Chem. Eng.*, **19**, 221 (2002).
6. T. J. Chung, M. C. Kim and C. K. Choi, *Korean J. Chem. Eng.*, **21**, 41 (2004).
7. E. H. Kim, S. W. Kwon and E. H. Lee, *Korean J. Chem. Eng.*, **19**, 305 (2002).
8. B. D. Leila and H. J. Fierz, *Hazard. Mater.*, **93**, 137 (2002).
9. S. J. Parulekar, *Chem. Eng. Sci.*, **53**, 2379 (1998).
10. S. A. El-Sayed, *J. Loss Prev. Process Ind.*, **16**, 249 (2003).
11. J. Kumar and S. Nath, *Chem. Eng. Sci.*, **52**, 3455 (1997).
12. T. Kotoyori, *J. Hazard. Mater.*, **A64**, 1 (1999).
13. S. Chervin and G. T. Bodman, *Thermochim. Acta.*, **392-93**, 371 (2002).
14. Y. W. Wang, C. M. Shu, Y. S. Duh and C. S. Kao, *Ind. Eng. Chem. Res.*, **40**, 1125 (2001).
15. A. A. Kossoy and T. Hofelich, *Pro. Saf. Prog.*, **22**, 235 (2003).
16. A. A. Kossoy and Y. Akhmetshin, *Pro. Saf. Prog.*, DOI: 10.1002/prs.10189 (2007).
17. N. A. Milas and A. Golubovic, *J. Am. Chem. Soc.*, **81**, 5824 (1959).
18. OSHA, Methyl Ethyl Ketone Peroxide Organic Method # 77, Occupational Safety and Health Administration, USA (1989).
19. K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).
20. Farkaas and Passaqlied, *J. Am. Chem. Soc.*, **72**, 3333 (1950).
21. G. Knorred, K. Maizusz and M. Emanueln, *Doklady Akad. Nauk S.S.S.R.*, **123**, 123 (1958).
22. T. Gunjan and B. Purnendu, *Ind. Eng. Chem. Res.*, **45**, 109 (2006).
23. B. G. Kwon and J. H. Lee, *Anal. Chem.*, **76**, 6359 (2004).
24. E. D. Black and E. Hayon, *J. Phys. Chem.*, **74**, 3199 (1970).
25. P. Maruthamuthu and P. Neta, *J. Phys. Chem.*, **82**, 710 (1978).
26. P. Y. Jiang, Y. Katsumura, M. Domae, K. Ishikawa, R. Nagaishi, K. Ishigure and Y. Yoshida, *J. Chem. Soc., Faraday Trans.*, **88**, 3319 (1992).