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Journal of Hazardous Materials 153 (2008) 1071–1077
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Effects of acetone on methyl ethyl ketone peroxide runaway reaction

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Received 20 March 2007; received in revised form 18 September 2007; accepted 18 September 2007
Available online 29 September 2007

Abstract

Runaway reactions by methyl ethyl ketone peroxide (MEKPO) are an important issue in Asia, due to its unstable structure and extensive heat release during upset situations. This study employed differential scanning calorimetry (DSC) to draw the experimental data for MEKPO 31 mass% and with acetone 99 mass% on three types of heating rate of 2, 4, and 10 °C/min; the kinetic and safety parameters were then evaluated via curve fitting. Through the reproducible tests in each condition, the results show that acetone is not a contaminant, because it could increase the activation energy (E_a) and onset temperature (T_o) when combined with MEKPO, which differs from the hazard information of the material safety data sheet (MSDS).

Keywords: Runaway reactions; Methyl ethyl ketone peroxide (MEKPO); Differential scanning calorimetry (DSC); Acetone; Kinetic and safety parameters

1. Introduction

Chemical industries widely apply organic peroxides as initiators and cross-linkers during polymerization, such as methyl ethyl ketone peroxide (MEKPO), di-*t*-butyl peroxide (DTBP), *t*-hexyl hydroperoxide, cumene hydroperoxide (CHP), and so on [1]. In practice, acetone is readily available for cleaning in various applications. Historically, many accidents have been incurred by MEKPO in Asia (Table 1); therefore, its unstable characteristics need to be understood thoroughly in order to alleviate the degree of hazard in manufacturing and operating processes. If a reaction is exothermic and the heat evolution in the system is greater than the heat loss, then the temperature will increase until all reactants are consumed, as reported by Zatka [2]. Kotoyori indicated that incidents involving ignition or explosion of thermally unstable substances may occur due to failure of temperature control in process vessels [3]. In a systematic study, we have attempted to elucidate the runaway reaction phenomena of MEKPO combined with acetone.

In this area of thermal analysis, many related calorimeters have been employed to discover the unstable materials. Yu et al. use C80D to demonstrate the hazardous material of asphalt-salt mixtures (ASM) [4]. Stoessel applies DSC to evaluate the thermal stability of nitro-aromatics, and then obtains the safety parameter of time to maximum rate (TMR) [5]. Miyake et al. use microcalorimetries for evaluating the thermal hazard of self-reactive substances of CHP in chemical processes [6]. The accelerating rate calorimeter (ARC) also has been applied to calculate the safety parameters reported by Whitmore and Wilberforce [7]. By vent sizing package 2 (VSP2), Tseng et al. demonstrate that MEKPO is a sensitive material, especially when mixed with inorganic acids [8] or contaminants [9]. Other measurement methods have been used in this area, including isoconversion methods for estimating the activation energy [10].

In this study, we attempted to elucidate the status of a runaway reaction for MEKPO in the presence of acetone. If acetone has

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0304-3894/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2007.09.099

Nomenclature

A	frequency factor (M^{1-n}/s)
C_p	specific heat capacity (J/g K)
E_a	apparent activation energy (kJ/mol)
ΔH	heat of reaction (J/g)
k	rate constant (M^{1-n}/s)
m	mass of reactant (mg)
n_i	reaction order (unitless)
Q	caloric capacity of measuring cell from exothermic substances (J/g)
R	gas constant (8.314 J/mol K)
T	temperature (°C)
TCL	time to conversion limit (day)
TMR	time to maximum rate (h)
T_0	exothermic onset temperature (°C)
ΔT_{ad}	adiabatic temperature rise (°C)
z	autocatalytic constant (unitless)

Greek letters

α_i	degree of conversion (unitless)
β	scanning rate (°C/min)
γ	degree of conversion for second and third stages (unitless)

Table 1
Selected severe thermal explosion accidents caused by MEKPO in East Asia [11]

Year	Location	Injuries	Fatalities	Hazard
1979	Taiwan (Taipei)	49	33	Explosion (storage)
1996	Taiwan (Taoyuan)	47	10	Explosion (tank)
1964	Japan (Tokyo)	114	19	Explosion
1978	Japan (Kanagawa)	0	0	Explosion
2000	Korea (Yosu)	11	3	Explosion
2001	China (Jiangsu)	2	4	Explosion
2003	China (Zhejiang)	3	5	Explosion

been mixed with MEKPO, the degree of hazard can be decreased compared with pure MEKPO.

2. Experimental setup

2.1. Standard procedure for preparation of MEKPO 31 mass% and acetone 99 mass%

MEKPO 31 mass% was purchased directly from Fluka Co., which had been stored in a refrigerator at 4 °C. Acetone 99 mass%, used as a diluent, was also stored in a refrigerator at 4 °C. After mixing of these two materials, the experimental data were determined by DSC three times in each condition. Afterwards, curve fitting was employed to model the kinetic and safety parameters. Mass ratio of MEKPO/acetone has been arranged and listed in Table 2.

2.2. Differential scanning calorimetry (DSC)

Temperature-programmed screening experiments were performed on a DSC (Mettler TA8000 system), and a measuring cell that can withstand relatively high pressure to approximately 100 bar (DSC 821^e) was used for the experiment. STAR^e software was used to obtain thermal curves [12]. For precise comparison of the results of curve fitting and achieving better thermal equilibrium, the scanning rate was set at 2, 4, and 10 °C/min, respectively [13]. The range of temperature rise was chosen from 30 to 300 °C during the excursion of the test in each condition.

3. Results

All of the experimental and curve fitting results are displayed in Tables 2, 3 and 4 (these mixture conditions were not used in our previous studies). Aside from the information raised by the literature and MSDS, our results indicated the inhibition phenomenon of acetone on the MEKPO runaway reactions.

4. Discussion

4.1. Curve fitting analysis

According to the experimental and curve fitting results, MEKPO is a thermally unstable material because of the weak O–O bond. There were three exothermic peaks during decompositions. The first peak belongs to an n-order reaction, followed by autocatalytic reactions for the second and third. Advantages of the method are demonstrated by Kossoy and Koludarova [14]. A complex model of consecutive reactions where the second and third stages were autocatalytic can be expressed by Eqs. (1)–(3):

1st stage:

$$\frac{d\alpha}{dt} = A_1 e^{-E_{a1}/RT}(1-\alpha)^{n_1} \text{—}n\text{-order reaction} \quad (1)$$

2nd stage:

$$\frac{d\gamma}{dt} = A_2 e^{-E_{a2}/RT}(\alpha-\lambda)^{n_2}(z+\gamma^{n_3}) \text{—autocatalytic reaction} \quad (2)$$

3rd stage:

$$\frac{d\gamma}{dt} = A_3 e^{-E_{a3}/RT}(\alpha-\lambda)^{n_4}(z+\gamma^{n_5}) \text{—autocatalytic reaction} \quad (3)$$

When MEKPO 31 mass% was combined with acetone 99 mass% at three different heating rates (2, 4, and 10 °C/min), all reactions indicated that the first exothermic onset temperature (T_0) increased from 35.4 to 38.1 °C, 43.6 to 79.2 °C, and 55.6 to 61.3 °C, respectively. The apparent activation energy (E_a) also had been reduced during the mixture conditions for the first peak; these phenomena can be readily seen in Figs. 1 and 2.

Table 2
Thermokinetic parameters derived from the DSC data on MEKPO 31 mass% and mixed with acetone 99 mass% for the first peak of the reaction

Sample	β (°C/min)	T_0 (°C)	E_a (kJ/mol)	n_1	n_2	A (s^{-1})	z	ΔH (J/g)
MEKPO 31 mass% (2.5 mg)	10	**55.6**	**136.5**	**1.1**	*	**43.2**	*	**68.7**
MEKPO 31 mass% (3.2 mg)	4	**43.6**	**119.3**	**0.9**	*	**36.5**	*	**65.6**
MEKPO 31 mass% (3.1 mg)	2	**35.4**	**117.8**	**0.8**	*	**36.9**	*	**65.5**
MEKPO 31 mass% (2.2 mg) + acetone 99 mass% (1.0 mg)	10	**61.3**	**138.0**	**1.0**	*	**42.9**	*	**76.2**
MEKPO 31 mass% (2.9 mg) + acetone 99 mass% (1.2 mg)	4	**79.2**	**184.1**	**0.8**	*	**55.9**	*	**57.4**
MEKPO 31 mass% (2.5 mg) + acetone 99 mass% (1.0 mg)	2	**38.1**	**120.2**	**0.7**	*	**37.8**	*	**66.3**

The first peak of the reaction. Calculated values based on experimental data from DSC tests. Estimated values are shown in bold. (*) Not applicable.

Table 3
Calculated thermokinetic parameters derived from the DSC data on MEKPO 31 mass% and mixed with acetone 99 mass% for the second peak of the reaction

Sample	β (°C/min)	E_a (kJ/mol)	n_1	n_2	A (s^{-1})	z	ΔH (J/g)
MEKPO 31 mass% (2.5 mg)	10	**78.4**	**1.1**	**0.2**	**18.5**	**0.0186**	**198.7**
MEKPO 31 mass% (3.2 mg)	4	**59.4**	**0.9**	**0.5**	**12.5**	$\mathbf{3 \times 10^{-3}}$	**312.6**
MEKPO 31 mass% (3.1 mg)	2	**51.8**	**0.9**	**0.7**	**10.1**	**0.0373**	**320.9**
MEKPO 31 mass% (2.2 mg) + acetone 99 mass% (1.0 mg)	10	**78.2**	**0.9**	**0.3**	**18.4**	$\mathbf{6.8 \times 10^{-3}}$	**129.4**
MEKPO 31 mass% (2.9 mg) + acetone 99 mass% (1.2 mg)	4	**114.3**	**1.3**	**0.3**	**28.9**	$\mathbf{1.5 \times 10^{-3}}$	**202.7**
MEKPO 31 mass% (2.5 mg) + acetone 99 mass% (1.0 mg)	2	**56.2**	**0.9**	**0.3**	**11.1**	**0.0142**	**284.7**

The second peak of the reaction. Calculated values based on experimental data from DSC tests. Estimated values are shown in bold. z: Autocatalytic constant [26].

One important parameter that was employed to understand the hazardous characteristics is the heat of reaction (ΔH). When acetone 99 mass% (about 1 mg) was doped into the test cell for combining with the MEKPO 31 mass%, the ΔH was reduced compared with the pure solution. Especially under a heating rate of 4 °C/min, the ΔH decreased from 65.6 to 57.4 J/g in the first peak. After the first peak was induced, the second and third peaks were classified as autocatalytic reactions, treated as unexpected reactions. The ΔH also decreased from 320.9 to 284.7 J/g, 312.6 to 202.7 J/g, and 198.7 to 129.4 J/g under the heating rates of 2, 4, and 10 °C/min, respectively. In terms of the third peak of each condition, the ΔH also was reduced while MEKPO was combined with acetone, as indicated in Table 4. All of the results demonstrate that an inhibitive reaction can be formed in mixing conditions. As far as T_0, ΔH, and E_a are concerned, these results were the first to be reported on these issues.

4.2. Safety parameters analysis

Practically speaking, many safety parameters could be employed to classify the degree of hazard for hazardous materials that is adopted, such as self-accelerating decomposition temperature (SADT) [15–18], temperature of no return (T_{NR}), and so on. According to the experimental results, since MEKPO has more than two exothermic peaks, both of these two safety parameters are not suitable for use in this study. In essence, time to maximum rate (TMR) is used for determining the degree of runaway reactions if an accident occurs. TMR was proposed by Townsend and Tou [19] in 1980, who derived convenient analytical expressions (Eqs. (4) and (5)) for calculation purposes:

$$\mathrm{TMR} = \frac{RT^2}{\mathrm{AE_a}\Delta T_{\mathrm{ad}}} \mathrm{e}^{-E_a/\mathrm{RT}} \tag{4}$$

$$\Delta T_{\mathrm{ad}} = \frac{Q}{C_p} \tag{5}$$

However, the formulas are valid only for simple single stage n-order reactions. In the case of more complex reactions, including autocatalytic reactions, TMR can be properly determined only by applying kinetics-base curve fitting. This method has been used in the present study.

From Figs. 3–5, when MEKPO was combined with acetone within the temperature range of 20–100 °C, the degree of hazard was decreased. Accordingly, pure MEKPO was more dangerous than the mixed ones.

Table 4
Calculated thermokinetic parameters derived from the DSC data on MEKPO 31 mass% and mixed with acetone 99 mass% for the third peak of the reaction

Sample	β (°C/min)	E_a (kJ/mol)	n_1	n_2	A (s^{-1})	z	ΔH [J/g]
MEKPO 31 mass% (2.5 mg)	10	**123.6**	**0.8**	**0.5**	**25.6**	**0.0124**	**483.3**
MEKPO 31 mass% (3.2 mg)	4	**130.8**	**1.1**	**1.7**	**29.2**	**0.0945**	**359.1**
MEKPO 31 mass% (3.1 mg)	2	**144.9**	**0.4**	**0.4**	**31.9**	**0.0711**	**373.3**
MEKPO 31 mass% (2.2 mg) + acetone 99 mass% (1.0 mg)	10	**103.7**	**1.1**	**1.1**	**21.4**	**0.0385**	**436.1**
MEKPO 31 mass% (2.9 mg) + acetone 99 mass% (1.2 mg)	4	**136.7**	**0.5**	**0.4**	**29.6**	**0.0162**	**234.8**
MEKPO 31 mass% (2.5 mg) + acetone 99 mass% (1.0 mg)	2	**122.1**	**0.4**	**0.6**	**26.1**	**0.0125**	**330.4**

The third peak of the reaction. Calculated values based on experimental data from DSC tests. Estimated values are shown in bold. z: Autocatalytic constant [26].

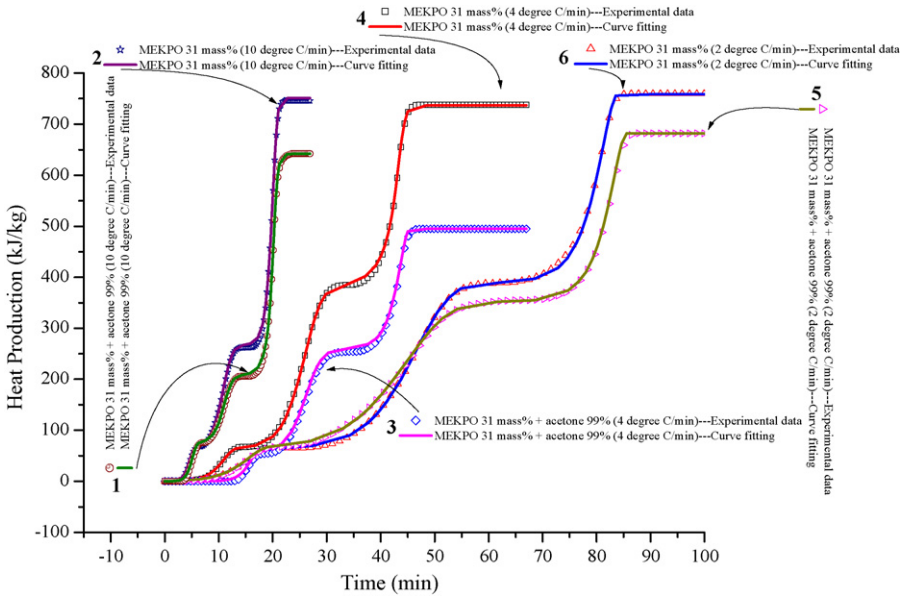

Fig. 1. Comparison of experimental data on heat production for MEKPO 31 mass% and mixed with acetone 99 mass% with kinetics-based curve fitting results ((1) MEKPO + acetone with scanning rate of 10 °C/min for experimental data and curve fitting; (2) MEKPO with scanning rate of 10 °C/min for experimental data and curve fitting; (3) MEKPO + acetone with scanning rate of 4 °C/min for experimental data and curve fitting; (4) MEKPO with scanning rate of 4 °C/min for experimental data and curve fitting; (5) MEKPO + acetone with scanning rate of 2 °C/min for experimental data and curve fitting; (6) MEKPO with scanning rate of 2 °C/min for experimental data and curve fitting).

For determining thermal stability, which is characterized by the time necessary to reach a certain level of conversion at certain constant temperature of time to conversion limit (TCL) [20], it was necessary to determine the stability of materials under storage or transportation conditions. From Figs. 6–8, within the temperature range of 20–100 °C, the results revealed that pure MEKPO was more unstable than in mixed conditions. This was contrary to the normal perception that acetone may exacerbate the severity of hazards incurred by MEKPO in terms of runaway reactions.

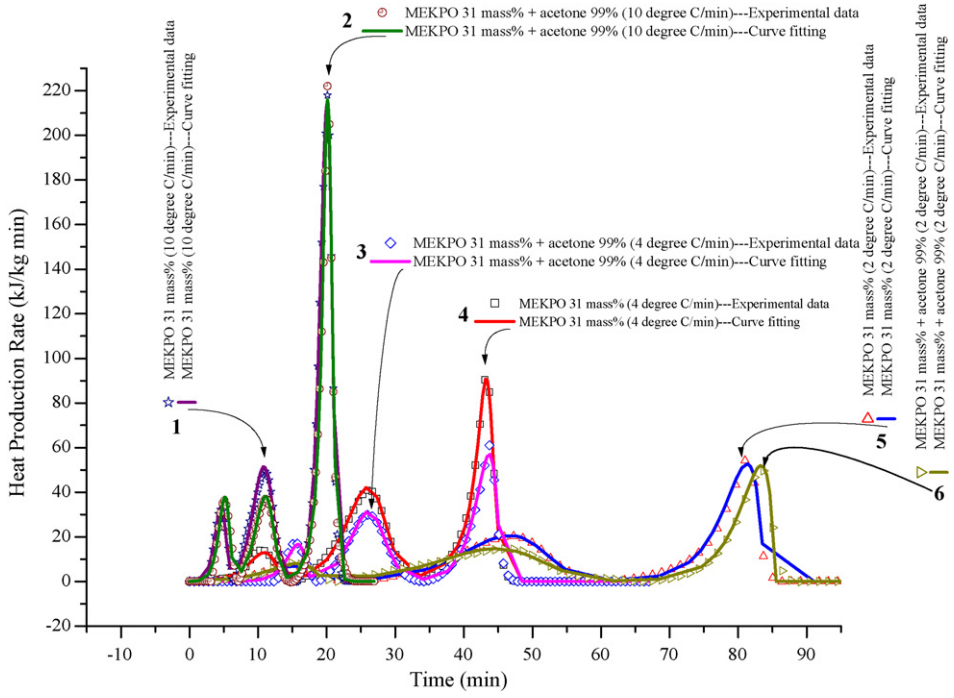

Fig. 2. Comparison of experimental data on heat production rate for MEKPO 31 mass% and mixed with acetone 99 mass% with kinetics-based curve fitting results ((1) MEKPO with scanning rate of 10 °C/min for experimental data and curve fitting; (2) MEKPO + acetone with scanning rate of 10 °C/min for experimental data and curve fitting; (3) MEKPO + acetone with scanning rate of 4 °C/min for experimental data and curve fitting; (4) MEKPO with scanning rate of 4 °C/min for experimental data and curve fitting; (5) MEKPO with scanning rate of 2 °C/min for experimental data and curve fitting; (6) MEKPO + acetone with scanning rate of 2 °C/min for experimental data and curve fitting).

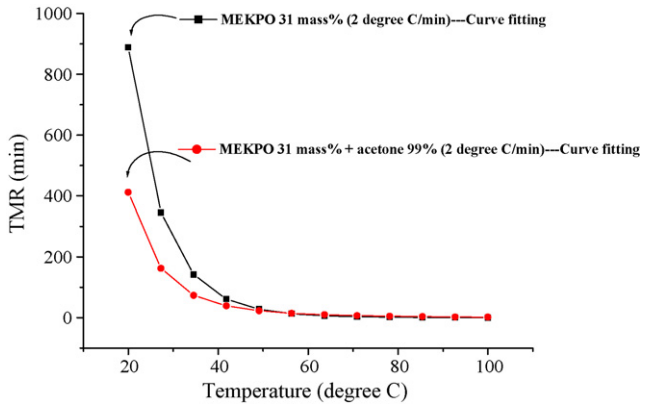

Fig. 3. TMR vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 2 °C/min.

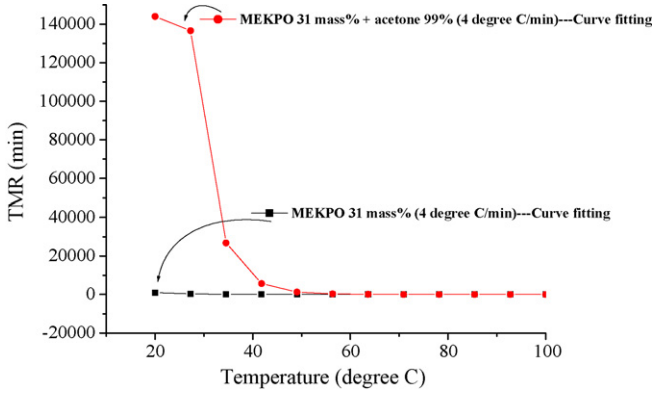

Fig. 4. TMR vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 4 °C/min.

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4.3. Reaction mechanism analysis

MEKPO has seven types of structures [21]. When MEKPO, bis-hydroperoxide, was heated gradually, it would decompose into several free radicals, as shown in Fig. 9 [22,23]. Based on the data of bond dissociation energy (BDE) listed in Table 5, enol radicals appear to be more stable ones [24,25]. When the decomposition of MEKPO is accompanied by acetone, as shown in Fig. 10, these free radicals then could either be transformed to more stable enol radicals, or produce less reactive nonperoxide intermediates (2-hydroperoxy-propan-2-ol or butane-2,2-diol). Thus, the rate of the decomposition of MEKPO is slowed down.

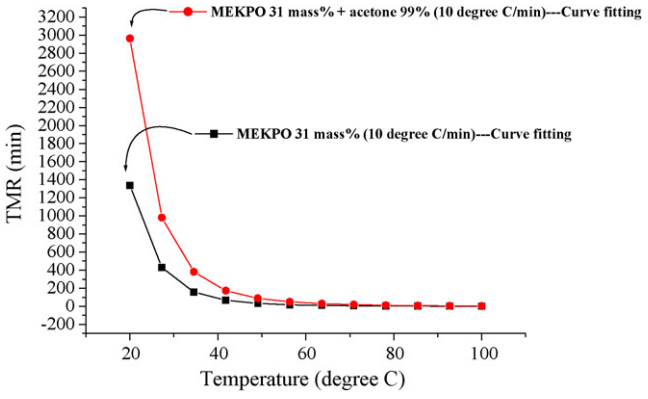

Fig. 5. TMR vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 10 °C/min.

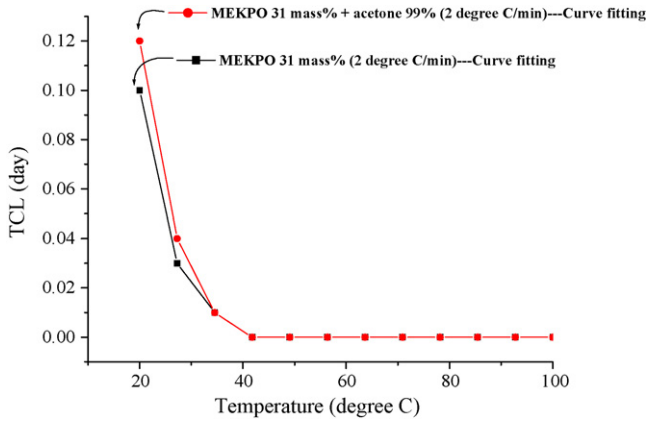

Fig. 6. Time to conversion limit (TCL) vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 2 °C/min.

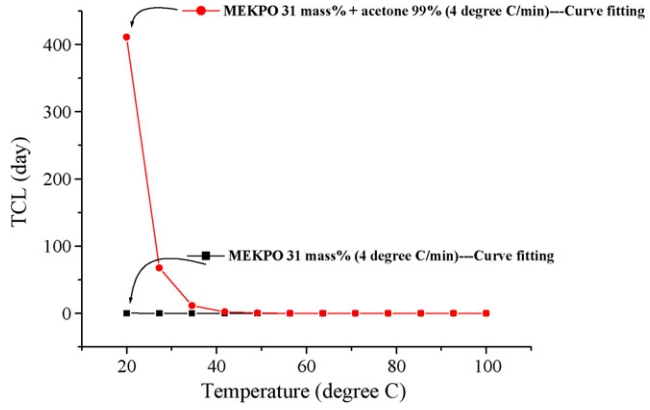

Fig. 7. Time to conversion limit (TCL) vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 4 °C/min.

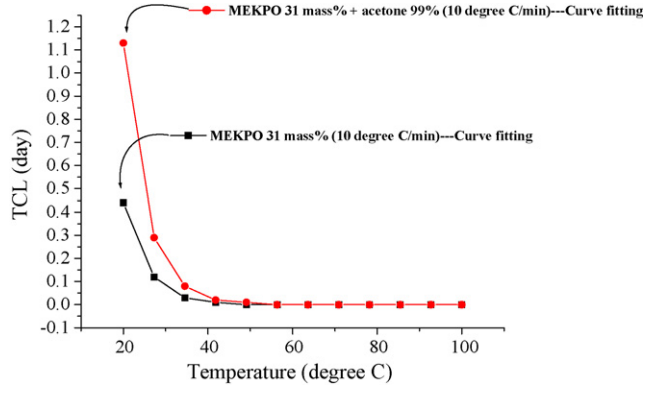

Fig. 8. Time to conversion limit (TCL) vs. temperature (kinetics-based curve fitting) for MEKPO 31 mass% and mixed with acetone 99 mass% with heating rate of 10 °C/min.

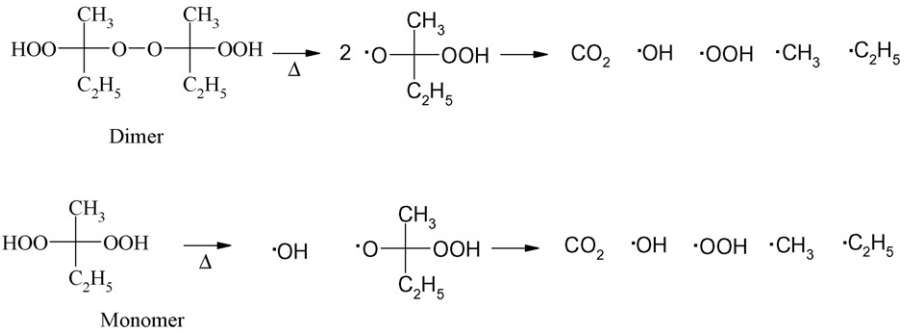

Fig. 9. Proposed decomposition mechanisms of pure MEKPO.

Table 5
Bond dissociation energies for MEKPO and acetone [25]

Bond	Dissociation energy (kJ/mol)	Bond	Average bond dissociation energy (kJ/mol)
CH_3—H	439	C—H	413
CH_3CH_2—H	420	C—C	348
HO—H	425	C—O	358
$CH_3C(O)CH_2$—H	401	O—O	146

$X-Y \underset{\Delta G=\text{energy released in combing radicals greater value means higher energy (more unstable) radical}}{\overset{\Delta G=\text{energy required to homolyse bond}}{\rightleftarrows}} X\cdot Y\cdot.$

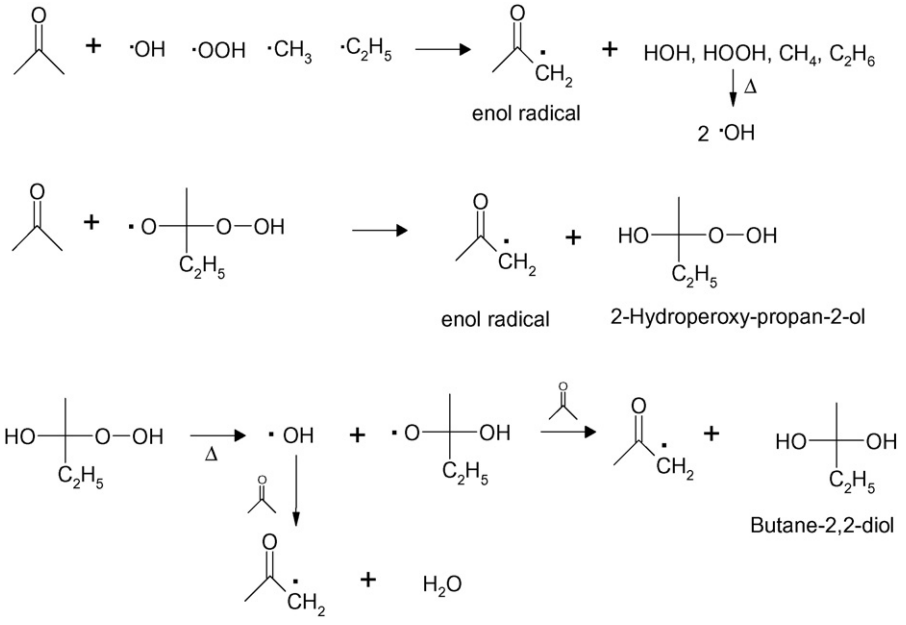

Fig. 10. Proposed reaction mechanisms of MEKPO combined with acetone.

5. Conclusions

A new study of runaway reactions on MEKPO 31 mass% combined with acetone 99 mass% was accomplished by DSC, and curve fitting–runaway reactions were explored. As far as ΔH, T_0, and E_a are concerned, acetone was found to be a stable solvent, which mitigated the degree of severity in terms of MEKPO thermal runaway. As such, it did not induce a dangerous reaction by MEKPO. On the other hand, it was not thermally reactive when mixed and was found to be capable of reducing ΔH. Such a modification in combining acetone with MEKPO may have played an important role in understanding the hazardous characteristics of pure MEKPO alone.

Acknowledgments

We are indebted to Dr. Arcady A. Kossoy of ChemInform Saint Petersburg (CISP), Ltd., St. Petersburg, Russia and Mr. Anthony M. Janeshek of Dow Chemical, Global Process Engineering, Freeport, Texas, USA, for their considerable technical assistance.

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