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Kinetics and hazards of thermal decomposition of methyl ethyl ketone peroxide by DSC☆

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Abstract

Differential scanning calorimetry (DSC) was applied to analyze thermal decomposition of methyl ethyl ketone peroxide (MEKPO). Thermokinetic parameters and thermal stability were evaluated. MEKPO decomposes in at least three exothermic decomposition reactions and begins to decompose at 30–32 °C. The total heat of decomposition is $1.26 \pm 0.03\,\mathrm{kJ\,g^{-1}}$. Thermal decomposition of MEKPO can be described by a model of two independent reactions: the first is decomposition of a less stable isomer of MEKPO, followed by decomposition of the main isomer, after which an exothermic reaction of the reaction products with the solvent, dimethyl phthalate. The results can be applied for emergency relief system design and for emergency rescue strategies during an upset or accident.

Keywords: Differential scanning calorimetry (DSC); Methyl ethyl ketone peroxide (MEKPO); Thermokinetic parameters; Thermal stability

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1. Introduction

Methyl ethyl ketone peroxide (MEKPO), which is a typical catalyst for the room temperature curing of unsaturated polyester resins with activators such as cobalt octoate, is also used as an initiator for polymerization reactions [1–4]. MEKPO is not a single compound, but a mixture of several isomers with the same name. Seven different configurations of MEKPO may exist, but monomer and dimer forms are prevalent in industry, as illustrated in Fig. 1 [5]. Worldwide, the annual consumption of MEKPO is ca. 22,000 t [6].

Thermal runaway incidents caused by organic peroxide are due to the peroxy group (–O–O–), which is intrinsically unstable and highly reactive [4,7–9]. In the past four decades, a large number of thermal explosions in Asia have occurred during transportation and production of MEKPO [4,10].

Within the organic peroxide class, sensitivity is dependent on active oxygen content, heat of decomposition (ΔH_d), activation energy (E_a), and decomposition kinetics [6]. Differential scanning calorimetry (DSC) is popular in evaluating not only the heat of reaction, but also the kinetics [7,8].

The kinetics model and parameters determined can be used to establish emergency relief system designs based on the method recommended by the Design Institute for Emergency Relief System (DIERS) under the auspices of the American Institute of Chemical Engineers (AIChE) as well as emergency rescue strategies with inherently safer approaches.

2. Experimental

2.1. Sample

MEKPO dimer 40 wt.% in dimethyl phthalate (DMP) was purchased from the Fluka Co. and then stored in a 4 °C refrigerator.

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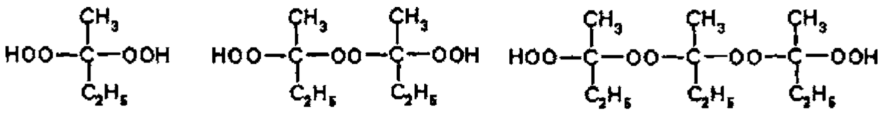
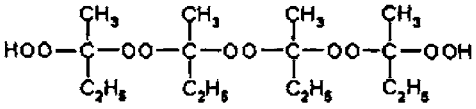


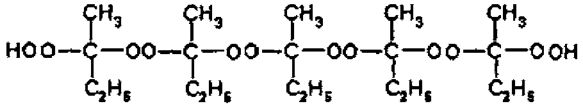
(a) MEKPO- I (Monomer)

(b) MEKPO- II (Dimer)

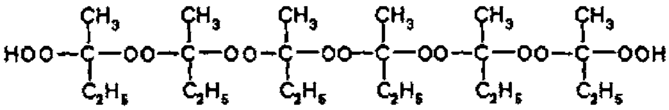
(c) MEKPO-III



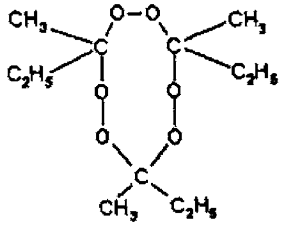
(d) MEKPO-IV



(e) MEKPO-V



(f) MEKPO-VI



(g) MEKPO-VII

Fig. 1. Structure of seven different configurations of MEKPO [5].

2.2. *Differential scanning calorimetry (DSC)*

Scanning experiments were performed on a Mettler TA8000 system coupled with a DSC821^e measuring cell that can withstand pressure up to about 100 bar. STAR^e software was used for acquiring curve traces [11]. A high-pressure sealed pan was used to avoid evaporation of the peroxide during scanning. Heating rates (β) were selected to be 2, 4 and 10 °C min^{-1}. The 10 °C min^{-1} heating rate is to attain a critical approach to thermal equilibrium [12,13]; the others are strictly for comparison purposes. Good consistency is obtained in three replications at each heating rate. To build up the numerical simulations for a kinetic model, ForK software (Formal Kinetic), developed by ChemInform Saint Petersburg (CISP) Ltd., was used [14].

3. Results and discussion

3.1. *Thermal hazard analysis*

Fig. 2 depicts the temperature (T) and rate of heat production ($\mathrm{d}Q/\mathrm{d}t$) for the thermal decomposition of MEKPO dimer 40 wt.% at different heating rates. MEKPO decomposition has at least three exothermic reactions, contrary to previous reports [4,15]. There is an exothermic reaction beginning at 30–32 °C and the heat of decomposition is 54 J g^{-1}. This has not been reported on previously, probably due to the low heat evolution in the first peak and differences in chemical composition and experimental conditions.

Table 1 displays the heat of decomposition (ΔH_d) and the exothermic onset temperature (T_o). Values of the ΔH_d agree with the literature results. The total ΔH_d was about

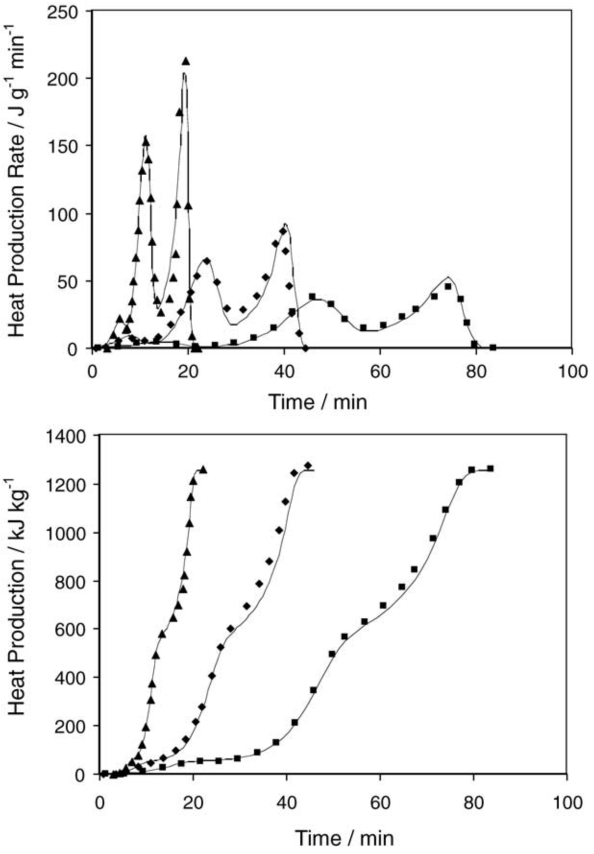


Fig. 2. Heat production rate and heat production vs. time for thermal decomposition of MEKPO dimer 40 wt.% by various heating rates. (■, ◆ and ▲) Data at the heating rates 2, 4 and 10 °C min^{-1}, respectively. Solid lines are simulated curves.

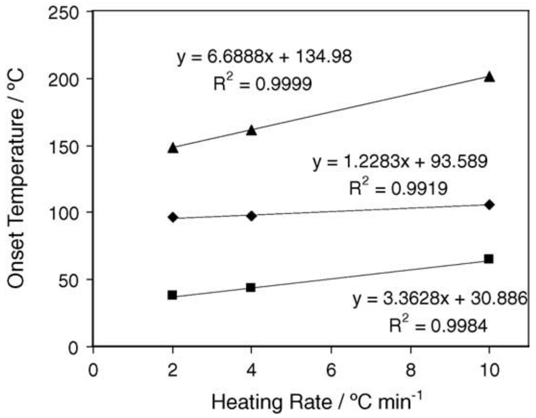


Fig. 3. Regression of heating rates vs. onset temperatures of the three peaks for MEKPO dimer 40 wt.%. (■, ◆ and ▲) Onset temperatures of first, second and third peaks, respectively.

$1.26 \pm 0.03\,\text{kJ g}^{-1}$. This large energy release ($>0.5\,\text{kJ g}^{-1}$) indicates that deflagration is a possibility [13]. T_o was extrapolated back to zero heating rate to approach true thermodynamic equilibrium values [16], as shown in Fig. 3. MEKPO should decompose slowly at 30–32 °C, as disclosed by our previous study for the monomer [4].

3.2. Kinetic analysis

To model thermal decomposition of the MEKPO dimer, it is hypothesized that the first peak corresponds to decomposition of a less stable isomer of MEKPO which is contained in the mixture in small amounts. The second reaction is the main isomer decomposing followed by the exothermic reaction of the reaction products with DMP.

$$\text{A} \rightarrow \text{B} \quad (\text{A}:\ \text{less stable isomer of MEKPO};\ \text{B}:\ \text{products})$$

$$\text{C} \rightarrow \text{D} \rightarrow \text{E} \quad (\text{C}:\ \text{MEKPO dimer};\ \text{D}:\ \text{intermediate and DMP};\ \text{E}:\ \text{products})$$

where the first reaction is autocatalytic and the second contains two consecutive stages, an *n*-order stage followed by an autocatalytic reaction. The third peak is much sharper and asymmetrical, indicating self-acceleration is taking place.

The corresponding mathematical model is represented by the system of ordinary differential equations, Eqs. (1)–(4) [17]

$$r_1 = \frac{\mathrm{d}\alpha_1}{\mathrm{d}t} = k_1(T)(1-\alpha_1)^{n_1}(z_1+\alpha_1)^{n_2} \tag{1}$$

$$r_2 = \frac{\mathrm{d}\alpha_2}{\mathrm{d}t} = k_2(T)(1-\alpha_2)^{n_2} \tag{2}$$

$$r_3 = \frac{\mathrm{d}\alpha_3}{\mathrm{d}t} = k_3(T)(\alpha_2-\alpha_3)^{n_{31}}(z_3+\alpha_3)^{n_{32}} \tag{3}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \sum_{i=1}^{3} Q_i^{\infty} r_i \tag{4}$$

where α_1, α_2 and α_3 are the conversion degrees of species A, C and D, respectively; r_i and Q_i^{∞} denote reaction rate and heat effect of the *i*th stage, $i = 1$, 2 and 3; $\mathrm{d}Q/\mathrm{d}t$ is the overall

Table 1
Heat of decomposition of the MEKPO dimer 40 wt.% at various heating rates of DSC test compared with other studies

	Peak, *i*th			Total	Yeh et al. [4]	Stull [15]
	1	2	3			
$-\Delta H_{d,i}$ (J g^{-1})	54 ± 5	483 ± 5	719 ± 15	1256 ± 25	1020[a]	588[b]

[a] The MEKPO sample is dimer form and 32 wt.% in DMP.

[b] The MEKPO sample does not have detailed information, including test conditions.

rate of heat generation. In addition, $k_i(T)$ obeys the Arrhenius temperature dependence of rate constant:

$$k_i(T) = k_{0i} \exp\left(\frac{E_{ai}}{RT}\right) \tag{5}$$

where k_{0i} and E_{ai} represent the frequency factor and activation energy of the ith stage. R is the gas constant ($=8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$).

Table 2 shows the kinetic parameters estimated by ForK on the basis of the three experimental curves, as can be also seen in Fig. 2.

3.3. Reactive hazard assessment

Two important practical indicators were determined to assess the hazardous characteristics of MEKPO: its thermal stability and adiabatic time to maximum rate ($\mathrm{TMR_{ad}}$).

Thermal stability of MEKPO was estimated by the kinetic model, as illustrated in Fig. 4. The results clearly show that MEKPO has very low stability and special measures should be taken to ensure safe long-term storage. From the hypothetical decomposition mechanism, the less stable isomer will decompose rapidly even at 0 °C: 100% conversion will be reached in less than 1 day. The main isomer can be stored at room temperature without serious losses (conversion does not exceed 10%) during about 4 months. Refrigerated warehouses and tanks should be used for storage and transportation of the product.

Adiabatic thermal explosion is important for practical discussions of safety because it represents the most dangerous case. Adiabatic time to maximum rate ($\mathrm{TMR_{ad}}$) can be used as an alternative to the use of a safety margin to define an upper safe temperature limit of a process. The usual way to determine $\mathrm{TMR_{ad}}$ under process conditions is to use the assumption of a zero-order reaction without taking account of product consumption. In the case of a complex reaction mechanism, especially when it involves autocatalytic stages, this simple approach is not applicable. Therefore $\mathrm{TMR_{ad}}$, as a function of the initial product temperature, was determined by using ForK by means of numerical simulation based on the complete model, as delineated in Fig. 5. According to the criteria for the assessment of an accident probability suggested from Stossel [18], the probability is considered to be high if $\mathrm{TMR_{ad}} < 8\ \mathrm{h}$. From this point of view, operational temperatures higher than 25 °C should be considered as inadmissible.

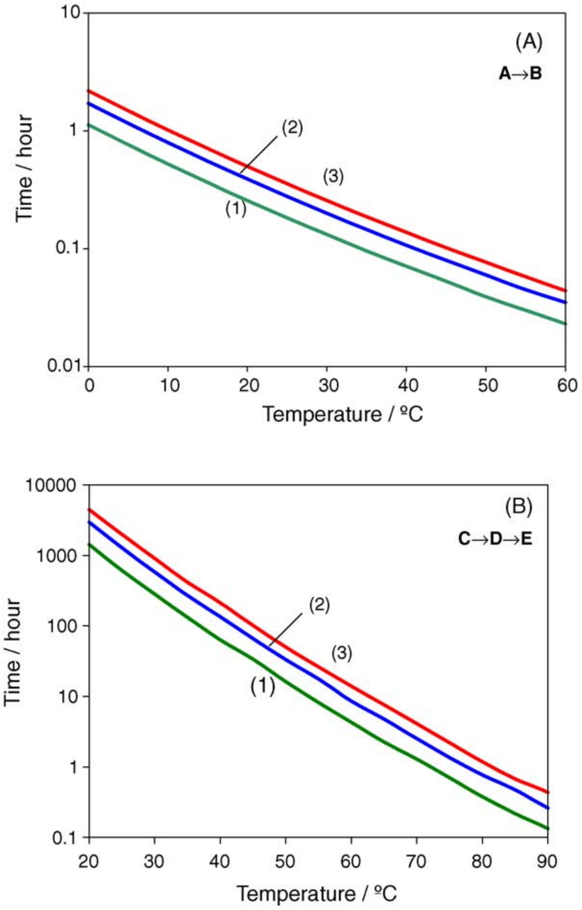


Fig. 4. Thermal stability analysis of MEKPO at room temperature: (A) and (B) were determined by conversion of A (minor isomer) and C (main isomer). (1), (2) and (3) represent the conversion of 5, 10 and 15%, respectively.

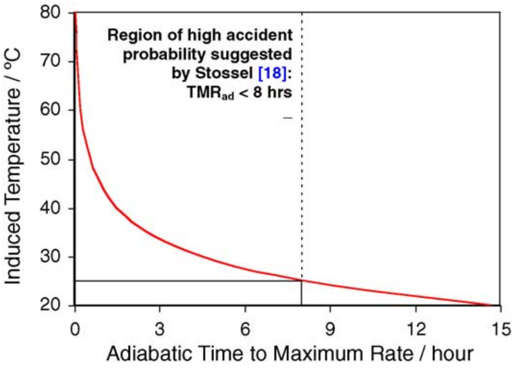


Fig. 5. Curve of adiabatic time to maximum rate ($\mathrm{TMR_{ad}}$) of MEKPO at room temperature.

Table 2
Kinetic parameters of the reaction model of 40 wt.% MEKPO dimer

$$r_1 = \frac{\mathrm{d}\alpha_1}{\mathrm{d}t} = 10^{5.35}\,\mathrm{e}^{-49{,}218/RT}(1-\alpha_1)^{0.884}(0.0161+\alpha_1)^{0.4882};\ Q_1^{\infty} = 53.694\ \mathrm{J\,g^{-1}}$$

$$r_2 = \frac{\mathrm{d}\alpha_2}{\mathrm{d}t} = 10^{13}\,\mathrm{e}^{-117{,}730/RT}(1-\alpha_2)^{1.043};\ Q_2^{\infty} = 483.206\ \mathrm{J\,g^{-1}}$$

$$r_3 = \frac{\mathrm{d}\alpha_3}{\mathrm{d}t} = 10^{4.45}\,\mathrm{e}^{-57{,}948/RT}(\alpha_2-\alpha_3)^{0.8602}(0.1606+\alpha_3)^{2.4209};\ Q_3^{\infty} = 719.502\ \mathrm{J\,g^{-1}}$$

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