

THERMAL DECOMPOSITION ANALYSIS OF ORGANIC PEROXIDES USING MODEL-FREE SIMULATION

A. Miyake^{1*}, K. Nomura¹, Y. Mizuta² and M. Sumino²

¹Department of Safety Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

²Science and Technology Research Center, Mitsubishi Chemical Co., Ltd., Kamoshida, Aoba-ku, Yokohama 236-8501, Japan

To understand better the thermal decomposition characteristics of organic peroxides, a C80 heat flux calorimeter was used and the decomposition pattern of cumene hydroperoxide and di-*tert*-butylperoxide were classified as auto-catalytic and n^{th} order reaction, respectively. Based on the scanning results with the C80 at several differing rates of heating, the thermal decomposition behavior of organic peroxides under isothermal storage at lower temperature was simulated with a model-free simulation. Simulated results showed that the calculated conversion of cumene hydroperoxide as a function of time was in good agreement with experimental data obtained with the TAM-III high sensitivity thermal activity monitor.

Keywords: model-free simulation, organic peroxide, thermal decomposition

Introduction

Organic peroxides (POs) have been widely used in chemical industries as initiators of polymerization, hardening or bridge formation. Since they are known for their self-reactive characteristics and many reports of accidents and investigations have been published [1–6], they are designated in materials handling regulations as dangerous goods. The hazardous nature of POs is characterized by their high reactivity of oxidation and the labile –O–O– bond in their structure which easily decomposes with external stimuli such as heat, and mechanical or high-density energies.

The conventional method for evaluating reactive chemicals consists of a literature survey, thermochemical calculation, and experimental estimation. While thermal analysis and calorimetry are useful tools for characterization of chemical substances for loss prevention and safety management, for the proper evaluation of substances, appropriate equipment is needed to match the specific characteristics of materials and their conditions.

To obtain a better understanding of the thermal decomposition characteristics of organic peroxides, constant heating and isothermal calorimetric analyses were performed. As an initial step a C80 heat flux calorimeter was used and the decomposition pattern of cumene hydroperoxide (CHP) with cumene solvent and di-*tert*-butylperoxide (DTBP) were investigated.

Based on the scanning results with the C80 using several differing heating rates, the behavior of these organic peroxides under isothermal storage at low

temperature was simulated with a model-free simulation [7]. Finally, the simulated results were compared with the isothermal experimental data obtained with the TAM-III high sensitivity thermal activity monitor and the validity of the simulation was assessed.

Experimental

Materials and methods

Materials used in this study were cumene hydroperoxide (CHP) [C₆H₅C(CH₃)₂OOH] 80 mass% (CHP 80) with cumene solvent and di-*tert*-butylperoxide (DTBP) [(CH₃)₃COOC(CH₃)₃] with a purity of 98 mass%. Both materials were commercially available technical grade reagents purchased from Aldrich Co., Ltd. and were used without further purification.

C80 heat flux calorimeter

Setaram C80, the heat flux calorimeter used in this study belongs to the Calvet type calorimeters distinguished by their accurate and reproducible calorimetric measurements. It is adapted to isothermal calorimeter as well as mixing calorimeter and temperature scanning calorimeter. In this study, the samples were heated in the SUS vessel with inner glass vessel up to 300°C with various heating rate and were also maintained at constant temperature with isothermal mode.

* Author for correspondence: atsumi@ynu.ac.jp

TAM-III thermal activity monitor

Thermometric TAM-III, the heat conduction calorimeter was used for isothermal study. Constant temperature is maintained within $2 \cdot 10^{-4} \text{ } ^\circ\text{C}$ per day, which allows heat flow in fraction of a micro Watt to be measured routinely. In this study, samples were dispensed into the disposable glass vial capped and then places in the measuring chambers. The measurements were conducted isothermally in the temperature range from 81 and $84 \text{ } ^\circ\text{C}$.

Results and discussion

The thermal hazard of organic peroxides determined with the heat flux calorimeter

Determination with a constant rate of heating

The thermal hazard of organic peroxides during heating was determined with a Setaram C80 heat flux calorimeter as follows. 0.5 g of CHP 80 or 0.4 g of DTBP was loaded into the quartz inner vessel which was placed in the SUS 316 pressure vessel to prevent

the catalytic effect of metal on the decomposition of the POs. The POs were heated up to $300 \text{ } ^\circ\text{C}$ with a heating rate of 0.1, 0.125, 0.25, 0.5 and 1.0 K min^{-1} in air or nitrogen at a pressure of 0.1 MPa. Figures 1 and 2 show the heat flow profiles of CHP 80 and DTBP under nitrogen at 0.1 MPa, and the activation energies of POs were determined by the Kissinger method to be 129 and 147 kJ mol^{-1} , respectively. From the results of the C80 measurement of maximum self-heat rate, heat of reaction, and activation energy with a constant rate of heating, the thermal hazard of CHP was found to be higher than that of DTBP.

Isothermal determination

Isothermal measurement was performed for CHP 80 and DTBP in air and nitrogen at a pressure of 0.1 MPa. Figures 3 and 4 show the heat flow profiles of 2.0 g of CHP 80 and 1.6 g of DTBP under isothermal conditions at different holding temperatures under nitrogen at 0.1 MPa.

From Fig. 3 the decomposition scheme of CHP 80 is found to be an auto-catalytic reaction, and from Fig. 4 that of DTBP determined to be an n^{th} order reaction [3].

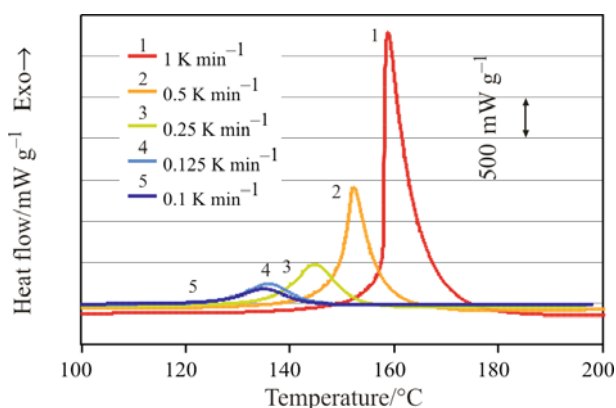


Fig. 1 Heat flow profiles of CHP 80 with C80 during constant heating in nitrogen

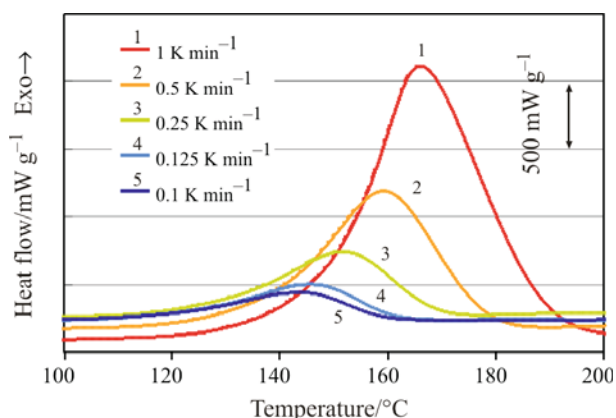


Fig. 2 Heat flow profiles of DTBP with C80 during constant heating in nitrogen

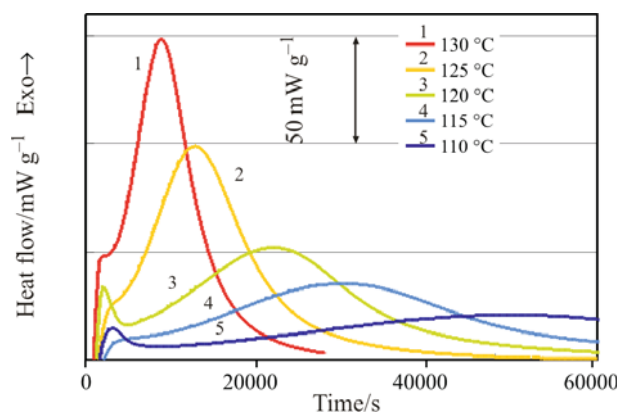


Fig. 3 Heat flow profiles of CHP 80 with C80 during isothermal condition in nitrogen

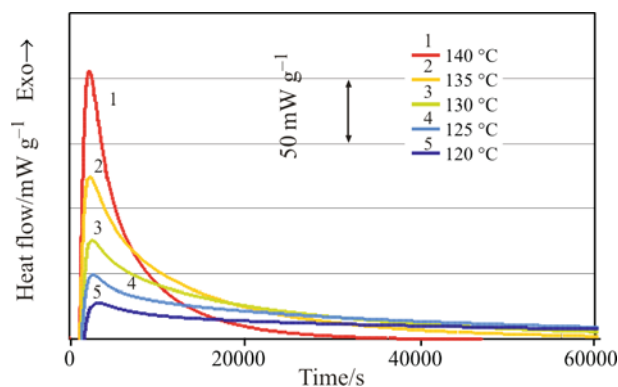


Fig. 4 Heat flow profiles of DTBP with C80 during isothermal condition in nitrogen

The reaction rate was calculated by the following equation.

$$q = -\Delta H \frac{dC}{dt} = \Delta H A f(C) \exp\left\{-\frac{E}{RT}\right\} \quad (1)$$

where q is the self-heat rate, ΔH is the heat of reaction, A and E are the pre-exponential factor and apparent activation energy, respectively, f is the model function, R is the gas constant, and T is the temperature. If $\Delta H A f(C)$ is assumed to be constant and independent of temperature, the following formula is obtained [8].

$$\frac{q_2}{q_1} = \frac{t_1}{t_2} = \exp\left\{\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\} \quad (2)$$

From selected values of time and heat flow in Figs 3 and 4, by using Eq. (2), the activation energies of CHP 80 and DTBP under nitrogen were determined to be 128 and 109 kJ mol⁻¹ respectively. The activation energy of CHP 80 showed good agreement with that determined with the C80 with a constant heating rate.

Isothermal measurement of thermal hazard with a thermal activity monitor

The isothermal measurement for CHP 80 was carried out with a Thermometric TAM-III high sensitivity thermal activity monitor at lower temperature than determinations with the C80. 0.5 g of CHP 80 was added to a glass vial and the vial was placed in the center bottom of a 20 mL SUS vessel in air or nitrogen at a pressure of 0.1 MPa at 81–84°C.

Figure 5 shows the isothermal determination of the thermal hazard of CHP 80 with the TAM-III under 0.1 MPa air. Although the temperature range is lower and the determination time thus longer, the heat flow profiles are similar in shape to those of obtained with the C80 and the reaction mechanism was found to be identical. The activation energy in air was determined to be 104 kJ mol⁻¹, a little less than that determined

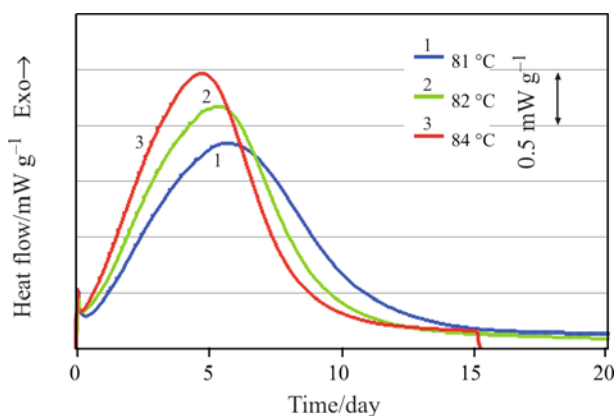


Fig. 5 Isothermal measurement of CHP 80 with TAM-III under 0.1 MPa air

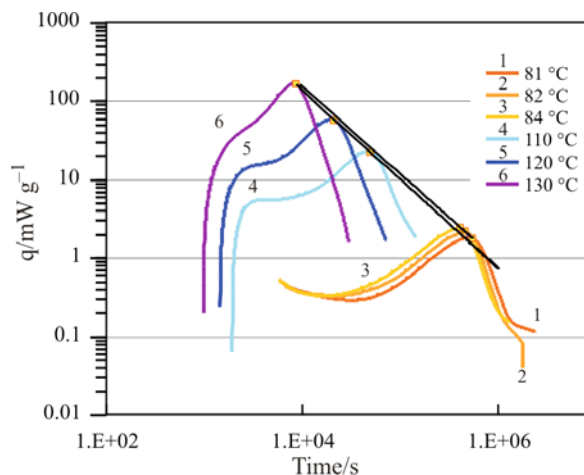


Fig. 6 Comparison of reaction rate between C80 and TAM-III at a conversion of 0.5

with the C80, i.e. 119 kJ mol⁻¹. The difference between determinations with the C80 and the TAM III is thought to be due to the higher sensitivity of the TAM III and the longer time required to reach the testing temperature in the experimental procedure.

Figure 6 shows the comparison between reaction rates obtained with C80 and those obtained with the TAM-III. The maximum rate is obtained for conversion of 0.5 g of CHP in each case. The linear fitting of results for the conversion of 0.5 g of CHP with the C80 shows good agreement with results with TAM-III. Using Eq. (2) confirmed the similarity of isothermal behavior at lower temperature determined with the TAM III and that determined with the C80 at higher temperature.

According to the similarity concept of the decomposition reaction [8], we tried to predict the self-heat rate and the time to $\alpha=0.5$ with the isothermal C80 data and compared this with the experimentally determined value using the TAM III. Table 1 shows the comparison of the predicted self-heat rate and time to $\alpha=0.5$ by C80 data with those by TAM III data. The predicted self-heat rate was 50–60% less than that of the TAM data and the predicted time to $\alpha=0.5$ was three times longer. Thus predicting the thermal hazard based on the similarity concept for isothermal behavior is not suitable for hazard assessment of CHP.

Table 1 Comparison of predicted self-heat rate and time to $\alpha=0.5$ by C80 and TAM III

Temp./°C	Self-heat rate/mW		Time to $\alpha=0.5$ /day	
	predicted by C80	TAM III	predicted by C80	TAM III
81	0.80	1.84	21.3	5.6
82	0.91	2.18	18.9	5.4
83	1.03	2.23	16.7	5.1
84	1.16	2.47	14.8	4.7

Model-free simulation

For the kinetic modeling we used the advanced kinetics and technology solutions (AKTS) software [7, 9]. The modeling is based on the use of the Arrhenius equation in the differential isoconversional method of Friedman that can be applied to elaborate heat flow signals from the C80. This numerical technique enables, after baseline optimization, an advanced and precise description of the decomposition reactions of chemicals. The reaction rate expressions generally have the following forms:

$$\frac{d\alpha}{dt} = A(\alpha)f(\alpha)\exp\left\{-\frac{E(\alpha)}{RT(t)}\right\} \quad (3)$$

$$\alpha = \frac{\Delta H}{\Delta H_{\text{total}}} \quad (4)$$

where $A(\alpha)$ and $E(\alpha)$ are the apparent pre-exponential factor and activation energy dependent on the reaction progress (=conversion) α , respectively. The accurate determination of the kinetic parameters and optimization of the baseline enable the correct fit of the experimental data. This advanced kinetic description is a prerequisite for prediction of the reaction progress under any new temperature profile. For the determination of the kinetic parameters of the process, a few signals collected with different heating rates were applied. Since peaks in the C80 curves shift towards higher temperatures when using higher heating rates, this set of data will contain the required information concerning the relationship between the conversions degree and temperature. This allows to determine the conversion dependence of the activation energy and pre-exponential factor, and hence to construct the appropriate non-parametric kinetic model.

Figures 7 and 8 show the simulated results of the conversion of CHP 80 compared with the experimentally analyzed data with the TAM-III. The conversion as a

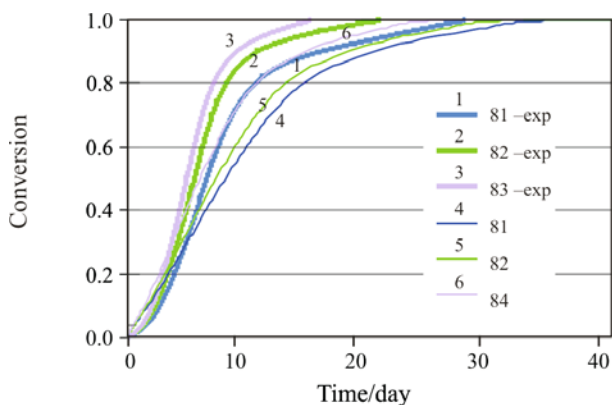


Fig. 7 Comparison of CHP 80 between experimental data of TAM-III and AKTS simulation based on heating scanning data with C80 under 0.1 MPa air atmosphere

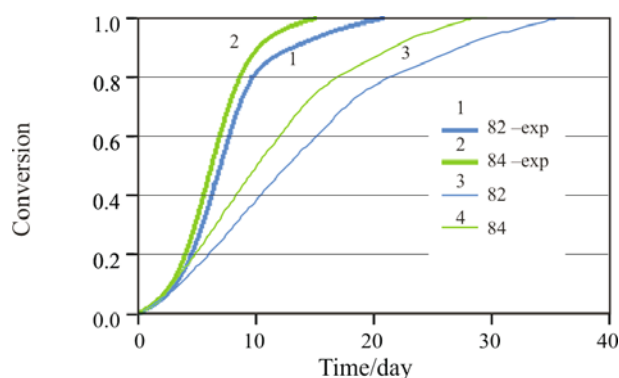


Fig. 8 Comparison of CHP 80 between experimental data of TAM-III and AKTS simulation based on heating scanning data with C80 under 0.1 MPa nitrogen atmosphere

function of time shows reasonable agreement in air, and a less accurate prediction is found in a nitrogen atmosphere. For instance, the time to $\alpha=0.5$ in air is measured as 5.4 but is 9.0 days by simulation. In nitrogen the time is measured as 7.0 but is 12.8 days by simulation. However the predicted value of the time to $\alpha=0.5$ in air based on the similarity concept was 18.9 days, and the simulated value using the model-free simulation was closer to the TAM-III data. Furthermore, isothermal simulation from the C80 constant heating data showed good agreement with the TAM-III data up to $\alpha=0.2$ and showed better prediction when used with C80 data at lower heating rates. Model-free simulation was concluded to be useful tool for prediction of isothermal behavior at lower temperature and it showed a reasonable agreement with high-sensitivity TAM-III data. Discussion of the disagreement between data and the details of the simulation procedure for obtaining optimized information will be the subject of further investigation.

Conclusions

From experimental investigation with a heat flux calorimeter and thermal activity monitor, the thermal decomposition of organic peroxides was investigated and following conclusions can be drawn:

- The decomposition schemes of two organic peroxides were classified by isothermal measurement showing that cumene hydroperoxide 80% decomposes in an auto-catalytic manner and di-*tert*-butylperoxide in an n^{th} order pattern.
- Predicted values of the self-heat rate and time to $\alpha=0.5$ from isothermal measurement with the Setaram C80 with the assistance of kinetic analysis did not show agreement with those determined by data at low temperatures obtained with the Thermometric TAM-III.

- Model-free simulation is a useful tool and the calculated conversion of CHP 80 as a function of time shows reasonable agreement with TAM-III data measured at lower temperatures.

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References

- 1 Center for Chemical Process Safety, Guidelines for safe storage and handling of reactive materials, 1995, AIChE.
- 2 J. Barton and R. Rogers, Chemical Reaction Hazards (2nd Ed.), 1995, IChemE.
- 3 T. Grever, Thermal Hazards of Chemical Reaction, Elsevier, 1994.
- 4 H. Y. Hu, C. M. Shu and Y. S. Duh, AIChE J, 47 (2001) 8.
- 5 K. Uetake, T. Fukazawa and N. Sakikawa, J. Jpn. Soc. Safety Eng., 18 (1979) 8 (in Japanese).
- 6 A. Miyake, T. Uchida, T. Ogawa and Y. Ono, J. Chem. Eng. Soc. Jpn., 21 (1995) 312 (in Japanese).
- 7 AKTS user' manual, 2006, AKTS.
- 8 M. Tamura, Ed., Handbook for Chemical Process Safety, Maruzen 2000.
- 9 B. Roduit, Ch. Borgeat, B. Berger, P. Folly, B. Alonso and J. N. Aebischer, J. Therm. Anal. Cal., 85 (2006) 195.

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