THERMAL HAZARD ANALYSIS OF CUMENE HYDROPEROXIDE USING CALORIMETRY AND SPECTROSCOPY

A. Miyake* and Y. O'hama

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

Organic peroxides have been widely used in industries and are known to be self-reactive chemicals. In this paper, thermal and infrared spectroscopic analyses were carried out to obtain a better understanding of the thermally hazardous behavior of cumene hydroperoxide (CHP) with cumene solvent. The temperature and heat flow profiles of different concentrations of CHP at scanning and isothermal conditions were measured with a small scale reaction calorimeter. Furthermore, probe type *in situ* infrared spectroscopic measurements were performed and the reaction mechanism will be discussed in regards to both energy release and product identification.

Introduction

Organic peroxides (POs) have been widely used in the chemical industry as initiators of polymerization, hardeners and cross-linking agents. Since they are also known for their self-reactive characteristics, illustrated by the many accident reports published [1–7], they are regulated as dangerous goods. The hazardous nature of POs is characterized by a high reactivity via oxidation. The –O–O– bond easily decomposes by external stimuli such as heat, mechanical or high density energies.

It is the purpose of this investigation to obtain a better understanding of the thermal decomposition behavior of POs. The temperature and heat flow profiles of different concentrations of cumene hydroperoxide (CHP) with cumene solvent at isothermal conditions were measured with a small scale reaction calorimeter. Furthermore, probe type *in situ* infrared spectroscopic measurements were performed and the influence of CHP concentration on the reaction was determined.

Experimental

Materials

CHP has been used as an initiator of polymerization of synthetic rubber and it also forms as an intermediate product of the phenol production process. CHP was commercially available from Aldrich Chemical Co. as a technical grade reagent with 80 mass% purity. Cumene was also commercially available from Wako Chemicals as a reagent first grade. Both chemicals were used without further purification and test samples were prepared as desired concentrations of CHP.

Methods

Scanning measurement

Calorimetric measurements were performed on a small scale reaction calorimeter, super-CRC™, of Omnical Technologies equipped with twin type 16 mL glass vessels. Super-CRC™ provides several functional modes such as reaction calorimetry or macro-type heat flow DSC and has a sensitivity of less than 10 μW and a small time constant of 100 s. Scanning test was performed with a heating rate of 1.0 K min⁻¹ for different concentration under 0.1 MPa air and onset temperatures and heats of reaction were determined.

Isothermal measurement

The isothermal measurements for different concentration and also different temperature were performed with super-CRC™ at 383, 388, 393, 398 and 403 K, and the influence of CHP concentration and holding temperature on the thermal decomposition behavior was studied. The rate constant and the activation energy were determined by means of kinetic analysis using the extent of reaction, i.e. conversion.

In situ infrared spectroscopy

In situ infrared spectroscopic monitoring was performed on a ReactionView™ system of

---

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

Remspec Co. equipped with a fiber-optic probe with a crystal ATR head. The detector module was coupled to and FTIR spectrometer. The crystal ATR head at the end of the probe was immersed in the 20 mL sample in the 50 mL glass vessel which was maintained at 398 K in order to obtain real time spectral information of species formed during the reaction. The probe was kept at 333 K or lower with the cooling unit to avoid damage due to heating. The spectra were collected at intervals of 30 s for a total of 1500 min as the thermal decomposition progressed. Each spectrum was collected at a resolution of 4 cm^{-1} and a rate of 3.5 scans s^{-1} for a total of 100 scans in the region of 1000–4000 cm^{-1}. And 3-dimensional graphics of wave number, absorbance as a function of time was obtained.

Results and discussion

Scanning measurement

Figure 1 shows the scanning measurement results with a heating rate of 1.0 K min^{-1} under 0.1 MPa air atmosphere. The onset temperature and heats of reaction are summarized in Table 1. Onset temperature showed almost the same temperature of 410 K in each sample, but CHP of lower concentration than 40% showed negative values of heat flow. It was due to the vaporization of cumene solvent and it was found that lower concentration CHP have lower risk of thermal runaway under open glass vessel.

Isothermal measurement

Influence of CHP concentration

CHP/cumene mixtures were prepared with a constant sample mass. The temperature was chosen to be 398 K which corresponds to the usual process temperature of phenol production.
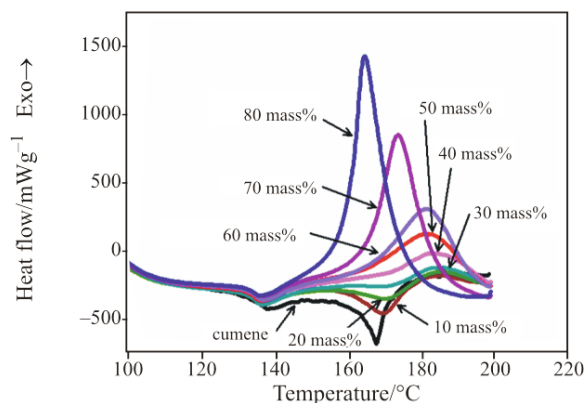

Fig. 1 Experimental results of scanning measurement of CHP with different concentration

Table 1 Experimental results of scanning measurement of CHP with different concentration

Sample	Heat of reaction ΔH/J g^{-1}	T_{onset}/ °C	q_{max}/ mW g^{-1}	T/ °C
80 mass%	930	137	1430	165
70 mass%	830	137	848	174
60 mass%	590	137	302	182
50 mass%	460	137	118	182
40 mass%	310	137	−10.5	184
30 mass%	120	137	−162	186
20 mass%	–	137	−161	186
10 mass%	–	138	−185	186

The sample mixture was heated to 398 K at a heating rate of 2 K min^{-1} with magnetic stirrer agitation. The temperature of the heating block was kept at 398 K until the heat flow profile returned to the baseline which indicated the end of the exothermic reaction. The reaction system was kept at atmospheric pressure through the ventilation needle.

Table 2 and Fig. 2 show the experimental results of the isothermal test of CHP at different concentrations. The heat flow of CHP 40 and 50 mass% showed a maximum value at the beginning followed by a constant decrease as CHP was consumed, which was a typical reaction type of an nth order decomposition [3]. The heat flow profiles of CHP 60, 70, 80 mass% showed an exothermic peak due to the CHP decomposition and the peak top was observed after several hours. The maximum heat flow increased and the time to the peak top shortened with increasing CHP concentration, which was a typical reaction type of an auto-catalytic decomposition [3].

These results show that the reaction type changes from an nth order reaction to an auto-catalytic reaction with an increase in CHP concentration. The maximum heat flow of CHP 70 mass% was twice as large as that of CHP 60 mass% and that of CHP 80 mass% was again twice as large as that of CHP 70 mass%. It is clear that the CHP concentration has a strong influence on the maximum heat flow in the auto-catalytic reaction. The thermal hazards of

Table 2 Experimental results of isothermal test of CHP with different concentration

	Max. heat release rate q_{max}/mW g^{-1}	Heat of reaction ΔH/J g^{-1}
CHP 80 mass%	85.2	337
CHP 70 mass%	23.7	247
CHP 60 mass%	12.0	200
CHP 50 mass%	5.99	178
CHP 40 mass%	5.49	132
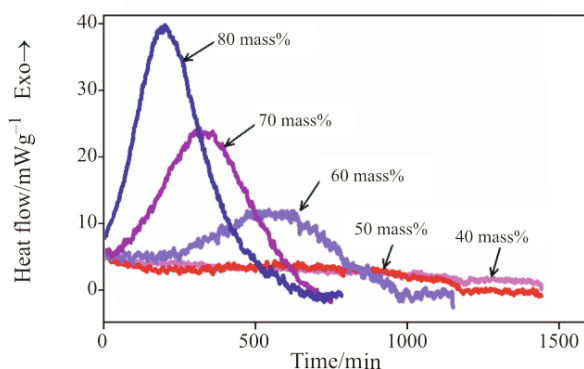
Fig. 2 Experimental results of isothermal test of CHP with different concentration

Fig. 3 Experimental results of isothermal test of CHP 80 mass% at each temperature

CHP concentrations less than 50 mass% were considered to be small.

Influence of holding temperature

1.0 g of CHP 80 mass% was heated to 383, 388, 393, 398 and 403 K at a heating rate of 2 K min^{-1} with magnetic stirrer agitation. Once the desired temperature was reached, the temperature of the heating block was kept constant and the heat flow was measured until the end of the exothermic peak.

Table 3 and Fig. 3 show the experimental results of the isothermal test of CHP 80 mass% at each temperature. Heat flow profiles showed exothermic peaks several hours into the experiment and an autocatalytic reaction was observed at each temperature. The reaction rate was affected by the holding temperature; the maximum heat flow increased and the time to the peak top shortened with the increase of the holding temperature.

The rate of reaction is expressed in the following formula [8]:

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

where q: rate of heat release (=heat flow), ΔH: heat of reaction, r: rate of reaction, C: concentration, E: acti-

Table 3 Experimental results of isothermal test of CHP 80 mass% at each temperature

T/K	Max. heat release rate q_{max}/mW g^{-1}	Time to q_{max} t_{max}/min	Heat of reaction ΔH/J g^{-1}
403	88.2	141	868
398	51.0	220	867
393	33.0	392	803
388	16.8	563	788
383	14.6	777	810
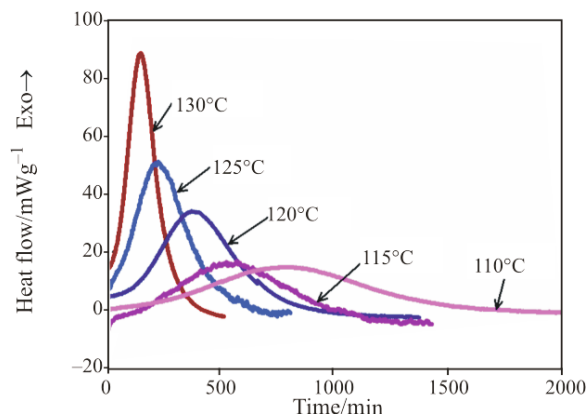
vation energy, R: universal gas constant, T: temperature. Here the initial concentration is defined to be 1.

From Eq. (1) the following formula is obtained:

$$\ln q = \ln\{\Delta HAf(C)\} - \frac{E}{RT} \quad (2)$$

Since the first term on the right side of Eq. (2) depends only on the concentration, it becomes constant if the rate of reaction and the temperature are constant. Here we assume that the reaction proceeds as a function of the extent of reaction, i.e., the fraction reacted, and the Arrhenius plot can be drawn using the degree of conversion shown in Eq. (3) instead of the extent of reaction.

$$u(t) = \frac{Q(t)}{Q} = \left(\frac{\int_0^t q(t)dt}{\int_0^\infty q(t)dt}\right) \quad (3)$$

where $u(t)$: degree of conversion as a function of time t, Q: total heat of reaction, $Q(t)$: heat of reaction at time t.

Therefore, the apparent activation energy is obtained from the slope of the plot of $\ln q$ vs. the reciprocal temperature. Based on the experimental plot, the apparent activation energy of thermal decomposition of CHP 80 mass% as a function of conversion was determined as shown in Table 4. It was suggested that the reaction mechanism changed at a conversion between 0.7 and 0.8, and those values were in good agreement with the published data [9–11].

In situ infrared spectroscopy

Infrared spectra of CHP 40 and 80 were collected continuously and the significant spectra were extracted.

Table 4 Apparent activation energy of CHP 80 mass% as a function of conversion

u	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E_a/kJ mol^{-1}	110	113	117	116	114	112	111	102	98
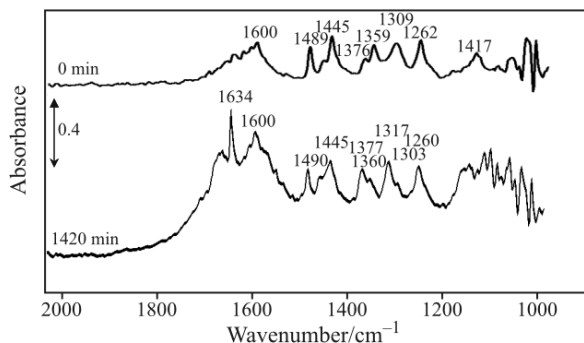
Fig. 4 Comparison of IR spectra of CHP 40 mass% at 0 and 1420 min from the beginning of measurement

Infrared spectra of CHP 40 mass%

The sample temperature was maintained at 398 K and no remarkable temperature change was observed throughout the experiment. Figure 4 shows selected spectra in the region of 1000–2000 cm^{-1} of CHP 40 mass% at 0 and 1420 min. Changes in the spectrum are obvious: the peak at 1309 cm^{-1} disappears, the peak at 1600 cm^{-1} grows, and the peaks of 1634–1685, 1317 and 1303 cm^{-1} appear. These peaks were found to grow and diminish as time progressed. Since the thermal decomposition of CHP 40 mass% progresses as an nth order reaction, these changes are reasonable. The peak at 1309 cm^{-1} is due to the weak absorption of CHP in the region of 1300–1320 cm^{-1}. Since the peaks at 1600 and 1634–1685 cm^{-1} are due to C=O stretches of substituted phenyl and aromatic ketones, respectively, the existence of acetophenone is the most probable. The peaks at 1317 and 1303 cm^{-1} also correspond to those of acetophenone. It is concluded that acetophenone is formed directly from CHP 40 mass% decomposition as the reaction progresses.

Infrared spectra of CHP 80 mass%

The sample temperature changed with the progress of the reaction, and 150 min after the sample reached 398 K, the temperature peaked at 399 K due to the reaction heat. This was followed by a decrease in temperature to 394 K until 500 min. This is an endotherm due to the gasification of acetone which was formed during the thermal decomposition of CHP.

Although, as in the case of CHP 40 mass%, spectral changes were observed in the region of 1000–2000 cm^{-1}, the change occurred in three stages.
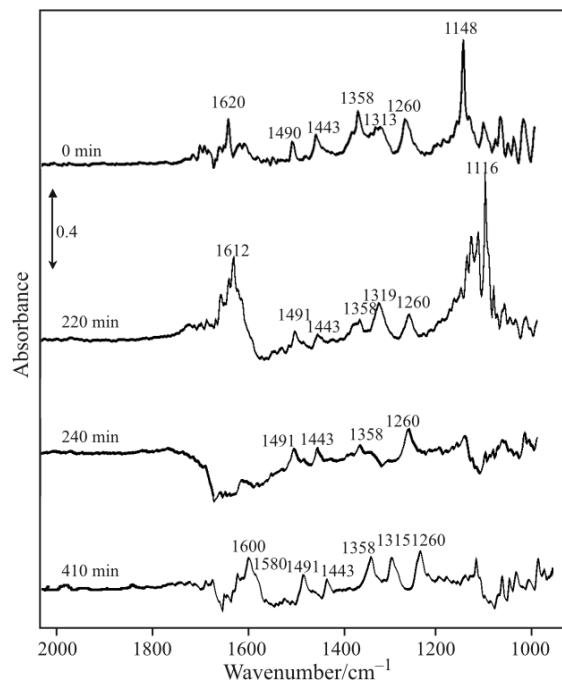

Fig. 5 Comparison of IR spectra of CHP 80 mass% at 0, 220, 240 and 410 min from the beginning of measurement

Figure 5 shows spectra of CHP 80 mass% at 0, 220, 240 and 410 min. In the first stage, 170 min from the beginning, noise at 1116–1143 and 1612–1630 cm^{-1} and peaks at 1319 and 1612 cm^{-1} appeared, showing a maximum absorbance at 220 min. The peak at 1612 cm^{-1} is due to C=C vibration and the peak at 1319 cm^{-1} and the noise of 1612–1630 cm^{-1} correspond to the peaks of α-methylstyrene. Since a temperature rise is observed at this stage, the decomposition of the sample is considered to progress via an autocatalytic reaction.

In the second stage, the peak due to α-methylstyrene disappeared after 240 min. Meanwhile the sample temperature began to decrease which is considered to be the formation and gasification of acetone which may be related to the disappearance of α-methylstyrene.

In the third stage, peaks at 1315, 1580 and 1600 cm^{-1} appeared after 340 min, showing a maximum absorbance at 410 min. These peaks correspond to acetophenone which is observed in Fig. 4. These peaks gradually diminish but remain until the end of the measurement time. Since the sample temperature also remains lower than the controlled temperature of

398 K, the formation of acetone lasts until the end of the reaction.

From heat flow profiles together with the infrared spectra, thermal decomposition of CHP 80 mass% is considered to proceed as follows [9]: the decomposition of CHP 80 mass% begins with the cleavage of the O–O and C–O bonds and α-methylstyrene is formed as an intermediate product in the early stages with a large heat of reaction. As α-methylstyrene diminishes, acetone is formed and gasified, followed by formation of acetophenone with other acids as the final products.

Conclusions

From our experimental thermal hazard analysis of CHPs with cumene solvent, the following conclusions can be drawn:

- The apparent activation energy of the exothermic decomposition of CHP 80 mass% varied with the conversion and the reaction mechanism was suggested to change as the reaction progress.
- CHP 40 mass% with cumene solvent decompose directly to acetophenone and organic acids with a small heat of reaction and are thermally less hazardous under the usual process conditions.
- CHP 80% with cumene solvent decompose in stages, first to acetone and α-methylstyrene via an autocatalytic reaction with a large heat of reaction, followed by a mild reaction to acetophenone and acids.
- *In situ* infrared spectroscopy with a fiber-optic probe is a useful tool for real time monitoring and analysis of the progress of reactions.

References

1 Center for Chemical Process Safety, Guidelines for Safe Storage and Handling of Reactive Materials, AIChE, 1995.
2 J. Barton and R. Rogers, Chemical Reaction Hazards (2nd Ed.), IChemE, 1995.
3 T. Grewer, Thermal Hazards of Chemical Reaction, Elsevier, 1994.
4 H. Y. Hou, 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 H. Y. Hou, Y. S. Duh, W. H. Lin and C. M. Shu, J. Therm. Anal. Cal., 85 (2006) 145.
7 J. M. Tseng, R. H. Chang, J. J. Horng, M. K. Chang and C. M. Shu, J. Therm. Anal. Cal., 85 (2006) 189.
8 H. G. Fisher, ERS Design using DIERS technology – DIERS project manual, AIChE/CCPS, 1992.
9 A. Miyake, T. Uchida, T. Ogawa and Y. Ono, J. Chem. Eng. Soc. Jpn., 21 (1995) 312 (in Japanese).
10 J. J. de Groot and F. Hupkens, IChemE Symposium Series, 1981, No. 68, 3/V:1.
11 M. Sumino, J. Lillis and Y. Iizuka, Proc. 36th Annual Conference of Japan Soc. Safety Eng., Yokohama 2002, pp. 187–190 (in Japanese).