Thermal decomposition behavior of cumyl peroxide measured by FT-IR

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The reaction is commonly controlled on the basis of the temperature and the pressure measured in a chemical reactor. However, some fire accidents occur in the chemical reactor when extraordinary reaction happens to progress in the routine temperature and pressure condition. It is difficult to know what reaction actually occurs because the chemical species is not observed. Information on the chemical species is important for the fire prevention to detect the runaway reaction in its early stages.
The purpose of this study is to investigate the hazardous evaluation method with a FT-IR (Fourier transform infrared spectrometer) in order to make the fire prevention and the safety handling countermeasures of chemical substances in the chemical reactor.

The FT-IR is used to measure the absorbance changes of chemical substances in the thermal decomposition.

Because absorbance is corresponded to concentration, the absorbance of chemical substances with the FT-IR is the important information to know the progress situation of reaction.
There is the possibility that the **FT-IR** can detect the change of absorbance before the thermal decomposition begins and accelerates.

There are some studies using the **FT-IR**. This study is characterized by the high pressure, simultaneous temperature and pressure measurement with the comparative large sample.


CHP (cumyl hydroperoxide) and DTBP (di-tert-butylperoxide) are organic peroxides and important reagents which play an important role as the initiators of polymerization in chemical industry.

CHP and DTBP are classified as the autocatalytic substance and the thermal decomposition substance, respectively.

DTBP is used as a standard material in the ARC (accelerating rate calorimeter) and the APTAC (automatic pressure tacking adiabatic calorimeter) measurements. DTBP was investigated in the previous paper.
CHP was selected as the sample for FT-IR experiments in this paper. The CHP decomposition was analyzed by the IR spectrum and the data of the temperature and the pressure measured simultaneously.

There are some studies on CHP decomposition.


Photography of Apparatus

- Pressure transducer
- Sample cell
- TC

pressure transducer

sample cell
Figure 1 Schematic measurement system
Apparatus

- The sample was put in a **glass sample vessel**.
- The **space volume** of the **pressure vessel** excluding the tip of the **fiber** was **30.3 cm³**.
- The **moisture** in the cooling air was **removed** to prevent the **accumulation** of water in the part where the fiber and the end of the **ZnS** crystal contacted because the **IR** spectrum of the accumulated water was detected.
- The **IR spectrum** data of the sample were stored in a **personal computer**.
- The **temperature and the pressure** data of the sample were stored in the other **personal computer**.
Sample

- CHP was used as the sample.
- The purity of CHP was from 81wt.% to 83wt.%.
- The sample mass was 5.0g.
- CHP was put in the glass vessel inside the pressure vessel.
- The cooling air and water was used to protect the fiber from heat.
Measurement Condition (1)

- The temperature and the pressure inside the close pressure vessel were measured simultaneously.
- Two types of test (the holding temperature (HT) test, and the ramp temperature (RT) test) were conducted.
- The heating of the pressure vessel started from the ambient temperature.
- The holding temperature (Th) was 134°C ~ 148°C.
- The temperature ramp rate of the pressure vessel was 2.1K/min.
- The temperature and the pressure data were stored every 0.01 (s) when the sample temperature reached 60°C.
Measurement Condition (2)

- The **IR spectrum** was measured by **ATR** (attenuated total reflection) measurement method in which the **ZnS crystal** was used.

- The **FT-IR spectrum** began to be stored every 30 seconds when the sample temperature reached 60 °C. This **period of 30 seconds** involved the time required to measure the **IR** spectrum.

- The **number of integration** of the **IR** spectrum was **sixteen** times.

- The **wavelength resolution** was **4 cm⁻¹**.

- The **IR spectrum** of the **sample** at **50° C** was used as a **background spectrum**.
# Table 1  Measurement results of temperature and pressure.

<table>
<thead>
<tr>
<th>No.</th>
<th>Test method</th>
<th>Holding temp.(Th) °C</th>
<th>Peak temp.(Tp) °C</th>
<th>Maximum temp. rate K/s</th>
<th>Maximum pressure MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HT</td>
<td>134</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>HT</td>
<td>143</td>
<td>160</td>
<td>78</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>HT</td>
<td>148</td>
<td>299</td>
<td>371</td>
<td>1.9</td>
</tr>
<tr>
<td>4</td>
<td>RT</td>
<td>156*</td>
<td>354</td>
<td>3008</td>
<td>4.2</td>
</tr>
</tbody>
</table>

HT: Holding temperature test  
RT: Ramp temperature test  
* : Heat onset temperature (To)

The peak temperatures (Tp, the maximum temperatures) of the HT test of 148 °C and the RT test was larger than that of the HT test of 143 °C.

Maximum temp. rate was calculated by data of every 0.1s.
The temperature peak began during the temperature rise. The peak temperature was 354℃ in the RT test. The maximum pressure was 4.2 MPa in the RT test. The heat onset temperature (To) was 156℃.

Figure 2 The time history of temperature in the HT test of 133℃ (No.1)

Figure 3 The time history of temperature in the HT test of 148℃ (No.3)

Figure 4 The time history of temperature in the RT test (No.4)

Figure 5 The time history of pressure in the HT test (No.3)
RESULTS AND DISCUSSION

Temperature and Pressure (Table 1)

- Figures 2 and 3 (HT Test)
- The temperature and pressure peak was not observed in 134°C of the holding temperature range. Because the temperature peak did not occur beyond 11000s in the other HT test of 133°C, the sample was heated at 2.4K/min approximately.
- The temperature and pressure peak was observed in 143°C of the holding temperature range in the HT test.
Temperature and Pressure (Table 1)

Figure 4 (RT Test),

- The **temperature peak** began during the temperature rise.
- The **peak temperature** was **354 °C** in the RT test.
- The **maximum pressure** was **4.2 MPa** in the RT test.
- The **heat onset temperature** (To) was **156 °C**.
- The **heat rate** was **3.1 K/min** at the heat onset temperature.
- The **peak temperatures** (Tp, the maximum temperatures) of the HT test of **148 °C** and the RT test was **larger** than that of the HT test of **143 °C**.
2981: methyl group
1266: COO group

CHP: before reaction

CHP: before reaction (expanded)
Figure 6: The spectrum of the solution at room temperature after CHP decomposed in the test of No.4.(RT)

- **Green peak**: increase peak
- **Red peak**: decrease peak
- **Noise peaks**: unexplained variations

- **2981 cm⁻¹ (CH)**
- **1290 cm⁻¹ (alcohol)**
- **1688 cm⁻¹ (AP)**
- **1127 cm⁻¹ (alcohol)**
- **1266 cm⁻¹ (CHP)**

**Chemical Structures:**
- Acetophenone (AP)
- Alcohol

Wavelength (cm⁻¹)
**Table 2  Assignment of spectrum**

<table>
<thead>
<tr>
<th>Wavelength (cm(^{-1}))</th>
<th>Group</th>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>2986</td>
<td>CH(_3)</td>
<td>Cumyl peroxide, CHP</td>
</tr>
<tr>
<td>1682</td>
<td>CO</td>
<td>Acetophenone, AP</td>
</tr>
<tr>
<td>1630</td>
<td>C=C</td>
<td>(\alpha)-methylstyrene, MS</td>
</tr>
<tr>
<td>1266</td>
<td>COO</td>
<td>CHP</td>
</tr>
<tr>
<td>1127</td>
<td>CO</td>
<td>Dimethylphenyl carbinol, DMPC</td>
</tr>
</tbody>
</table>
The decomposition behavior of CHP was examined by measuring spectrum changes under the progress of the reaction.

The background of this spectrum was the CHP solution before CHP decomposed.

There are the noise peaks for absorbance of carbon dioxide in $2360\text{cm}^{-1}$ and for no permeation of the optical fiber in $2170\text{cm}^{-1}$.

Absorbance below zero indicates that CHP was consumed due to the CHP decomposition.
The essential reaction paths and products were made as the following chemical equations referring to the reference literature.

\[
\text{PhC(CH}_3\text{)}_2\text{OOH} + \text{PhC(CH}_3\text{)}_2\text{H} \rightarrow 2\text{PhC(CH}_3\text{)}_2\text{OH} \rightarrow 2\text{PhC(CH}_3\text{)}=\text{CH}_2 + 2\text{H}_2\text{O} \quad \text{Eq(1)}
\]

\[
\text{PhC(CH}_3\text{)}_2\text{OOH} \rightarrow \text{PhCOCH}_3 \quad \text{Eq(2)}
\]

Ph means the phenyl group \((\text{C}_6\text{H}_5^-)\).

When cumene exists, CHP becomes dimethylphenyl carbinol (DMPC) in the CHP decomposition in Eq(1).
IR Spectra of CHP and decomposition products (3)

- Dimethylphenyl carbinol (DMPC) dehydrates and it becomes $\alpha$-methylstyrene in Eq(1).
- When cumene does not exist, acetophenone (AP) and methyl alcohol are generated in the CHP decomposition in Eq(2).
- The minus peak near 1266 cm$^{-1}$ is assigned to the COO group of CHP.
- The minus peak near 2986 cm$^{-1}$ is assigned to the methyl group.
- The minus peak near 3350 cm$^{-1}$ is assigned to the peroxide group.
IR Spectra of CHP and decomposition products (4)

- This peak near $3350\text{cm}^{-1}$ was not used in the spectrum analysis because this wavelength range involved the hydroxyl group of alcohol and this peak was broad.
- The absorption peak of $1682\text{cm}^{-1}$ was assigned to the carbonyl group of acetophenone(\textit{AP}) after the CHP decomposition.
- The absorption peak of $1630\text{cm}^{-1}$ was assigned to double bond of $\alpha$-methylstylene(\textit{MS}) after the CHP decomposition.
- The absorption peak of $1127\text{cm}^{-1}$ was assigned to the CO group of dimethylphenyl carbinol(\textit{DMPC}) after the CHP decomposition.
The minus peak of 1266 cm$^{-1}$ (CHP) became large when the temperature increased. It indicated CHP decreased when the decomposition progressed.

The peak of 1127 cm$^{-1}$ (DMPC) became large when the temperature increased in the HT tests. It indicated dimethylphenyl carbinol (DMPC) increased when the decomposition progressed.
The absorption change was related with the change of the concentration of chemical species.

- The minus peak of 1266 cm\(^{-1}\) (CHP) became large when the temperature increased. It indicated CHP decreased when the decomposition progressed.

- The peak of 1127 cm\(^{-1}\) (DMPC) became large when the temperature increased in the HT tests. It indicated dimethylphenyl carbinol (DMPC) increased when the decomposition progressed.
Figure 8  The change of the absorption spectrum from 1500cm$^{-1}$ to 1850cm$^{-1}$ with the elapsed of time in the test of No.3(HT).

The peaks of 1630cm$^{-1}$ (MS) and 1682cm$^{-1}$ (AP) increased simultaneously in the holding time of the HT tests. The peak of $\alpha$-methylstyrene (MS) appeared before the peak of acetophenone (AP) in the other HT test(133 oC).
Figure 9  The change of the absorption spectrum from 1500cm\(^{-1}\) to 1850cm\(^{-1}\) with the elapsed of time in the test of No.4(RT).

The peak of 1630cm\(^{-1}\) (MS) was not clear in the RT test of No.4. It indicated the production rate of \(\alpha\)-methylstyrene was smaller than that of acetophenone.
The peaks of 1630 cm\(^{-1}\) (\(\alpha\)-methylstyrene, MS) and 1682 cm\(^{-1}\) (acetophenone, AP) increased simultaneously in the holding time of the HT tests.

The peak of \(\alpha\)-methylstyrene (MS) appeared before the peak of acetophenone (AP) in the other HT test (133 °C).

The peak of 1630 cm\(^{-1}\) (MS) was not clear in the RT test of No.4. It indicated the production rate of \(\alpha\)-methylstyrene was smaller than that of acetophenone.
The decrease of the absorption of 2986 cm\(^{-1}\) (CHP) and 1266 cm\(^{-1}\) (CHP) already began from 100 °C in both tests. This result was the same as the other HT and RT tests. CHP decreased in proportion to the sample temperature until the peak temperature.

The absorbance was obtained by subtracting the measured baseline of spectrum from the absorbance of the measured peak because the baseline changed by the sample temperature. The absorbance data did not involve the data since the peak temperature. The absorbance is corresponded to the concentration of chemical species. The slope of absorbance can be regarded to be corresponded to the change rate of chemical species.
Figure 11  The relationship between the temperature and the absorbance regarding to No.4(RT) before the peak temperature.

It showed the decomposition of CHP already began from 100 oC in RT and HT tests. The decomposition productions of CHP were accumulated before the peak temperature.
Decomposition of CHP (1)

Figures 10 and 11

- This absorbance was obtained by subtracting the measured baseline of spectrum from the absorbance of the measured peak because the baseline changed by the sample temperature.
- The absorbance data did not involve the data since the peak temperature.
- The absorbance is corresponded to the concentration of chemical species.
- The slope of absorbance can be regarded to be corresponded to the change rate of chemical species.
- The decrease of the absorption of 2986 cm\(^{-1}\) (CHP) and 1266 cm\(^{-1}\) (CHP) already began from 100 °C in both tests.
  
  This result was the same as the other HT and RT tests.
- CHP decreased in proportion to the sample temperature until the peak temperature.
Decomposition of CHP (2)

It showed the decomposition of CHP already began from **100 °C**. The decomposition productions of **CHP** were accumulated before the peak temperature.

The decrease of **CHP** was measured in the liquid phase. The increase of **acetophenone** was measured in the liquid phase. The increase of acetophenone was corresponded to the decrease of **CHP**. These results showed the decomposition of **CHP** occurred in the **liquid phase**.
The results of CHP were compared with those of DTBP.

DTBP: spectrum change (1000-1600 cm⁻¹)

- Acetone is produced when DTBP decomposes.

DTBP ramp test 2K/min
DTBP: spectrum change (1600-2000cm\(^{-1}\))

DTBP ramp test  2K/min

ΔAbs.: 各ベースラインを基準とした吸光度の増減を調べる
Decomposition of CHP (3)
Comparison with CHP and DTBP results

The **common points** were as follows:

1. The decrease of CHP and DTBP of the start chemicals was found before the decomposition product was detected.

2. CHP and DTBP decreased in **proportional** to the sample temperature. The decrease rate against the sample temperature was almost **constant**.

The **different points** were as follows:

1. There were **two main paths** in the CHP decomposition (product: DMPC and AP).

2. There was **one main path** in the DTBP decomposition (product: acetone).

3. The increase rate of acetophenone of the decomposition product **increased** compared with that of the onset exotherm after the temperature peak occurred.

4. The increase rate of acetone of the decomposition product was **constant** compared with that of the onset exotherm after the temperature peak occurred.
Figure 12 The time history of the absorbance change in the No.1 test (HT).

The decrease of CHP already began before the sample temperature reached the holding temperature in all HT tests.
The decrease of CHP already began before the sample temperature reached the holding temperature in all HT tests.
Figure 14 The time history of the absorbance change in the No.3 test (HT).

CHP continued to decrease in the holding time of the sample temperature. Acetophenone and dimethylphenyl carbinol increased during the holding temperature.
The increase of absorbance of 1682 cm⁻¹ (AP) and 1127 cm⁻¹ (DMPC) increased rapidly when the peak temperature appeared in No.2(HT), No.3(HT) and No.4(RT) tests.
The decrease of CHP already began before the sample temperature reached the holding temperature in all HT tests.

CHP continued to decrease in the holding time of the sample temperature. Acetophenone and dimethylphenyl carbinol increased during the holding temperature.

The increase of absorbance of 1682 cm\(^{-1}\) (AP) and 1127 cm\(^{-1}\) (DMPC) increased rapidly when the peak temperature appeared in No.2(HT), No.3(HT) and No.4(RT) tests.
In the results with the peak temperature of No2, No.3 (HT tests) and No.4 (RT test), acetophenone and dimethylphenyl carbinol rapidly increased with a large increase rate when the sample temperature reached the peak temperature. CHP rapidly decreased with a large decrease rate when the sample temperature reached the peak temperature.
Decomposition of CHP (7)

The rapid absorbance change of acetophenone, dimethylphenyl carbinol and CHP corresponded to the peak temperature. An amount of absorption change of acetophenone was larger than those of dimethylphenyl carbinol and CHP.

The peak of CHP(1266 cm⁻¹) increased in No2, No3 and No.4 after the peak temperature. Its peak was not so reliable after the peak temperature. Its peak was influenced by the peak of acetophenone because it was near the large peak of acetophenone which continued to increase largely after the peak temperature.
The decomposition of CHP began before acetophenone was produced. The decrease rate of CHP was almost the same during the holding temperature.

It was thought that the intermediates of CHP decomposition production was accumulated and decomposed violently at the peak temperate when the intermediates concentration was beyond the certain limit value.

The detection of acetophenone could be the index of the fire prevention to predict the runaway reaction.
It was predicted that the generation of the peak temperature was caused by the acetophenone production reaction because the amount of generation of acetophenone is the largest after the peak temperature.

The decomposition of No.2 (HT) test was not more violent than that of No.3 (HT) test because CHP was consumed in the holding time.
The essential **CHP decomposition mechanism** was proposed as the following **chemical equation** referring to the reference literature.

\[
\text{PhC(CH}_3\text{)}_2\text{OOH} \rightarrow \text{PhC(CH}_3\text{)}_2\text{O}^\bullet + \text{OH}^\bullet \quad \text{Eq}(3)
\]

\[
\text{PhC(CH}_3\text{)}_2\text{O}^\bullet + \text{PhC(CH}_3\text{)}_2\text{H} \rightarrow \text{PhC(CH}_3\text{)}_2\text{OH} + \text{PhC(CH}_3\text{)}_2\text{O}^\bullet \quad \text{Eq}(4)
\]

\[
\text{PhC(CH}_3\text{)}_2\text{OH} \rightarrow \text{PhC(CH}_3\text{)}=\text{CH}_2 + \text{H}_2\text{O} \quad \text{Eq}(5)
\]

\[
\text{PhC(CH}_3\text{)}_2\text{O}^\bullet \rightarrow \text{PhCOCH}_3 + \text{CH}_3^\bullet \quad \text{Eq}(6)
\]

The break of the **COO** group was the **initiation of CHP decomposition**.

- When the **holding** temperature was **134°C** in the **HT** test of **No.(1)**, the **Eq(4)** and **Eq(5)** were the **main reactions**.
- There was **no peak temperature** when the hold time continued for more than **2 hours**.
When the other HT tests and the RT test were conducted, \text{Eq}(6) (\text{AP produced}) began with \text{Eq}(4) (\text{DMPC produced}) and \text{Eq}(5) (\text{MS produced}).

When \text{PhC(CH}_3\text{)}_2\text{O}^\bullet \text{regarded as the reaction intermediate was accumulated enough to generate the large heat, Eq}(6) occurred and the sample temperature reached the peak temperature \text{Eq}(4) and \text{Eq}(5) competed with \text{Eq}(6).

In the temperature range near 150°C, \text{Eq}(6) was the main reaction compared with \text{Eq}(4) and \text{Eq}(5).

When \text{CHP} was consumed by \text{Eq}(4) and \text{Eq}(5), the peak temperature may be small (see No(2) HT test). There was no peak temperature when the hold time continued for more than 2 hours.

It was suggested the decomposition reaction with the large heat generation was the reaction of \text{Eq}(6).
CONCLUSIONS

(1) The absorbance of the methyl and the COO group of CHP began to decrease before acetophenone of the decomposition products was detected. Acetophenone increased slightly in the holding time. The production reaction of acetophenone was the main reaction when the temperature peak occurred. The detection of acetophenone was useful for the fire prevention to predict the runaway reaction.

(2) The increase of dimethylphenyl carbinol, α-methylstyrene and acetophenone was measured with the decrease of CHP. It was elucidated that the decomposition of CHP occurs in the liquid phase.