

Thermal decomposition of di-tert-butylperoxide measured with calorimeter

Yusaku Iwata*[†]

*National Research Institute of Fire and Disaster, 4-35-3 Jindaijihigashi-machi, Chofu-shi, Tokyo, 182-8508 JAPAN
Phone: +81-422-44-8331

[†]Corresponding author: iwata@fri.go.jp

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Abstract

The thermal decomposition of di-tert-butyl peroxide (DTBP) was investigated with a differential scanning calorimeter (DSC) and a high sensitivity calorimeter (C80) in this report. DTBP is one of the organic peroxides and used as standard sample of the accelerating rate calorimeter. The heat of reaction of the DTBP/toluene solutions with various mass and concentrations were examined with the DSC. The relationship between the sample mass of various DTBP concentrations and the converted heat of reaction of pure DTBP per one gram (ΔH_{convd}) was examined. The ΔH_{convd} values of the small mass were larger than the values of the large mass when the samples from 5 wt% to 20 wt% of DTBP concentration were measured. The similar tendency of ΔH_{convd} was obtained in the C80 measurements. When the sample mass was almost constant in the DSC measurement, the measured ΔH_{convd} value decreased against the increase of DTBP concentration. The reduction rate of ΔH_{convd} of small sample mass was larger than that of large sample mass. The ΔH_{convd} value should be constant though the sample mass and concentration were changed. It is considered that the decomposition reaction of the vapor generated from DTBP/toluene solution occurred in the sample vessel of the DSC and C80. The ratio of the free volume in the sample vessel against the sample volume is introduced to explain the ΔH_{convd} values of various mass and concentrations measured with the DSC and the C80. It is elucidated that the reaction of vapor of DTBP/toluene solution plays important role in the thermal decomposition.

Keywords: differential scanning calorimeter, high sensitive calorimeter, heat of reaction, thermal decomposition

1. Introduction

Exothermal reaction is quantitatively measured with various calorimeters in order to evaluate the reaction hazard. For example, differential scanning calorimeter (DSC) is used as a hazardous evaluation method of the self-reactive substance in the Japanese Fire Service Law. The sample of the amount of about 1–10 mg is used in DSC. The high sensitivity calorimeter (C80) can measure the small generation of heat that cannot be detected with DSC. The measurement is conducted with the sample amount of about 0.5–5 g in C80. The data obtained with C80 is more reliable than those of DSC when the number of thermocouples and the heating rate method are taken into consideration.

The sample amount strongly influences on the exothermal behavior and the hazardous evaluation. In this

study, the relationship between the total amount of heat generation measured with DSC and C80 and the sample mass were examined using di-tert-butyl peroxide (DTBP) in this report. DTBP used in measurement is one of the organic peroxides and used as standard sample of the accelerating rate calorimeter^{1)–4)}.

2. Experimental

2.1 Apparatus

The total amount of heat generation were measured with the DSC and the C80 in the heat ramp measurement. The temperature range was from 25 to 250 °C. Potassium nitrate (KNO₃) and DTBP/toluene solution were used as the sample. KNO₃ was used to examine the accuracy of the heat value obtained by the DSC and the C80 when the samples with various mass were measured.

2.1.1 DSC

The heat rate was $5 \text{ K}\cdot\text{min}^{-1}$. The sample mass of KNO_3 was from 3.09 to 34.69 mg. The sample mass of DTBP/toluene solution was from 0.73 to 13.35 mg. The sample container of DSC was the close cell made of stainless steel. The volume of sample cell was 0.02 cm^3 , approximately.

2.1.2 C80

The heat rate was $0.1 \text{ K}\cdot\text{min}^{-1}$. The sample mass of KNO_3 was from 0.1 to 3 g. The sample mass of DTBP/toluene solution was from 0.85 to 6.10 g. The sample container of C80 was the close cell made of stainless steel. The volume of sample cell was 8.6 cm^3 , approximately.

2.2 Sample

KNO_3 of the special grade was purchased from Wako Pure Chemical Industries, Ltd. DTBP was purchased from NOF Corporation. Purity of DTBP is 98 %. Toluene of the special grade was purchased from Kanto Chemical CO., Inc. DTBP concentrations used in measurements were 5 wt%, 10 wt% and 20 wt%.

3. Results and discussion

3.1 DSC

When the mass of KNO_3 was varied in the DSC measurement, whether the heat value was influenced was examined. When the height of the sample inside the sample container was high, there is a possibility that the measured heat value becomes small due to the difficulty of heat conduction in the vertical direction. The volume of KNO_3 was from $1.46\text{--}16.44 \times 10^{-3} \text{ mL}$ because the density of KNO_3 was $2.11 \text{ g}\cdot\text{cm}^{-3}$.

The DSC curve of KNO_3 had the absorption peak. The amount of heat absorption at the phase transition temperature of 402K (128.9°C) was $49.98 \text{ J}\cdot\text{g}^{-1}$. Figure 1 shows the relationship between the sample mass and the amount of the heat absorption. The amount of the heat absorption was almost constant though the sample mass changed. The averaged value of the amount of heat absorption was $50.64 \text{ J}\cdot\text{g}^{-1}$. This value was almost the same as the reference value ($49.85 \text{ J}\cdot\text{g}^{-1}$)⁵⁾. The heat value obtained by the DSC was not influenced by the volume of sample.

Figures 2 and 3 show the DSC curves of DTBP 10 wt%/toluene solution (DTBP 10 wt%) and DTBP 20 wt%/toluene (DTBP 20 wt%) when the sample mass was changed from 0.73 mg to 11.92 mg. The horizontal axis is temperature ($^\circ\text{C}$). The vertical axis is heat flow (mW).

The DSC curve had two peaks in the temperature range. The ratio of the peak area of the shoulder peak to the main peak after the shoulder peak became smaller when the sample mass became larger. This tendency was observed similarly in the DTBP 5 wt%/toluene solution (DTBP 5 wt%) and DTBP 20 wt% solution.

Figure 4 shows the relationship between the mass of sample with various concentrations and the heat of reaction in the DSC measurement. The heat of reaction ΔH_{intake} is the value per one gram of the measured sample. The unit of ΔH_{intake} is $\text{J}\cdot\text{g}^{-1}$. The ΔH_{intake} value is the sum of

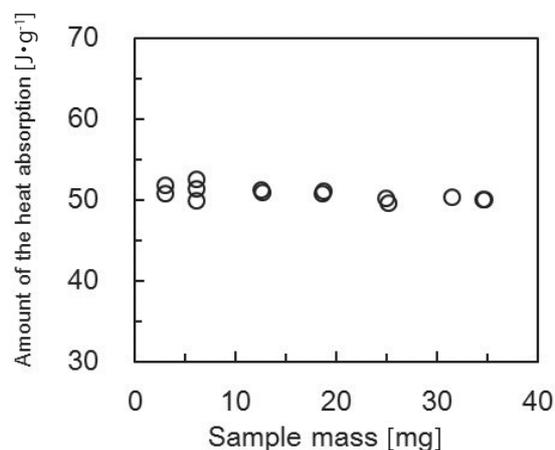


Figure 1 The relationship between the sample mass of KNO_3 and the amount of the heat absorption.

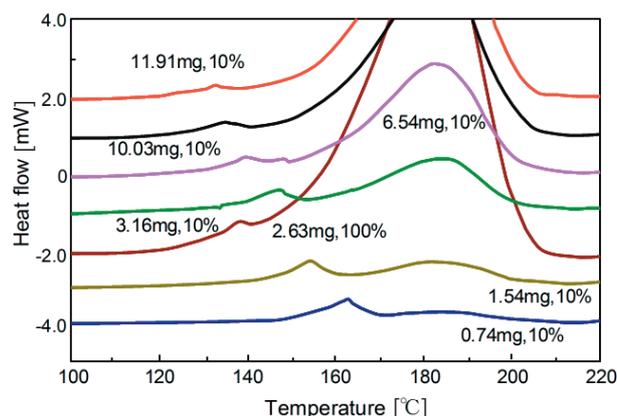


Figure 2 The DSC curves of DTBP 10 wt%/toluene solution and DTBP 100 wt% when the sample mass is changed from 0.74 mg to 11.91 mg. Heat rate: $5.0 \text{ K}\cdot\text{min}^{-1}$.

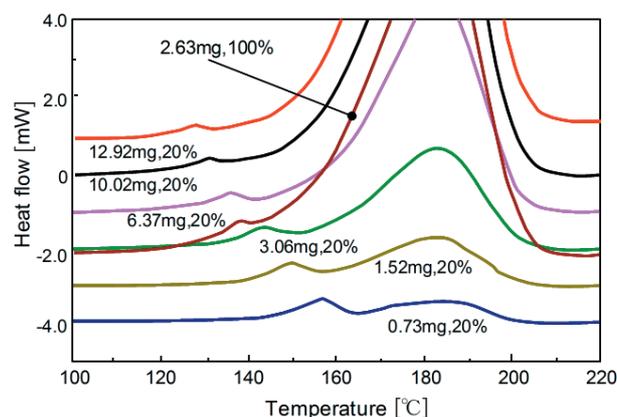


Figure 3 The DSC curves of DTBP 20 wt%/toluene solution and DTBP 100 wt% when the sample mass is changed from 0.73 mg to 12.92 mg. Heat rate: $5.0 \text{ K}\cdot\text{min}^{-1}$.

the amount of heat of the shoulder peak and the amount of heat of the main peak.

The ΔH value for each DTBP concentration decreased when the sample mass increased to about 5 g. The decrease ratio of ΔH to the sample mass became smaller when the DTBP concentration became larger.

Figure 5 shows the relationship between the sample mass of various DTBP concentrations and the converted

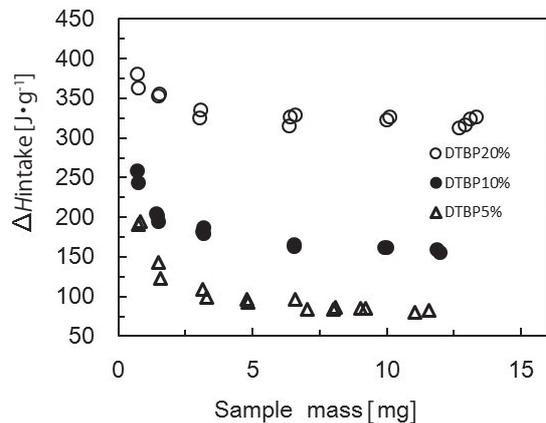


Figure 4 The relationship between the mass of sample with various concentrations and the heat of reaction per one gram of the measured sample in the DSC measurement.

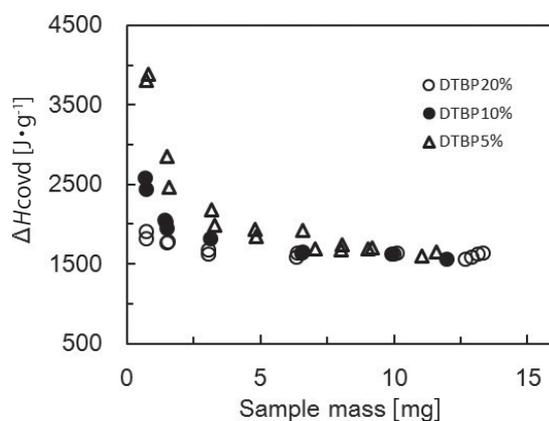


Figure 5 The relationship between the sample mass of various DTBP concentrations and the converted heat of reaction of pure DTBP per one gram (ΔH_{convd}) in the DSC measurement.

heat of reaction ΔH_{convd} . ΔH_{convd} is the value per one gram of DTBP in the sample. The unit of ΔH_{convd} is $\text{J}\cdot\text{g}^{-1}$. The ΔH_{convd} values of the small mass were larger than the values of the large mass samples for each DTBP concentration were measured. The ΔH_{convd} became almost constant though the DTBP concentrations were different when the sample mass was above about 5 g.

Figure 6 shows the relationship between DTBP concentration and ΔH_{convd} . The ΔH_{convd} values of DTBP 5 wt% and DTBP 10 wt% were higher when the sample masses were small. For examples, the ΔH_{convd} of DTBP 10 wt% was $2,036 \text{ J}\cdot\text{g}^{-1}$ (sample mass: 1.46 g). The ΔH_{convd} of DTBP 20 wt% was $1,778 \text{ J}\cdot\text{g}^{-1}$ (sample mass: 1.56 g). The ΔH_{convd} values for DTBP 20 wt% were not influenced by the sample mass compared with the sample of the other DTBP concentrations.

3.2 C80

The relationship between the sample mass and the amount of the heat absorption of KNO_3 was examined in the C80 measurement. The amount of the heat absorption was almost constant as well as the case of the DSC though the sample mass was varied. The averaged value of the amount of heat absorption was $50.70 \text{ J}\cdot\text{g}^{-1}$. The heat value

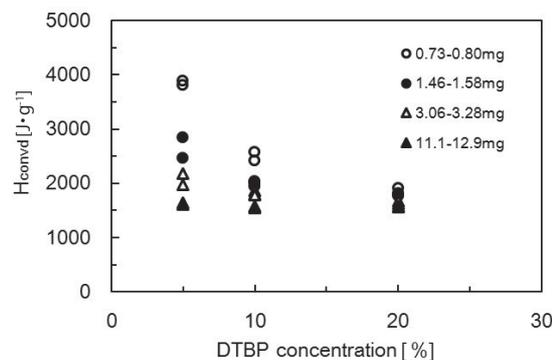


Figure 6 The relationship between DTBP concentration and ΔH_{convd} in the DSC measurement.

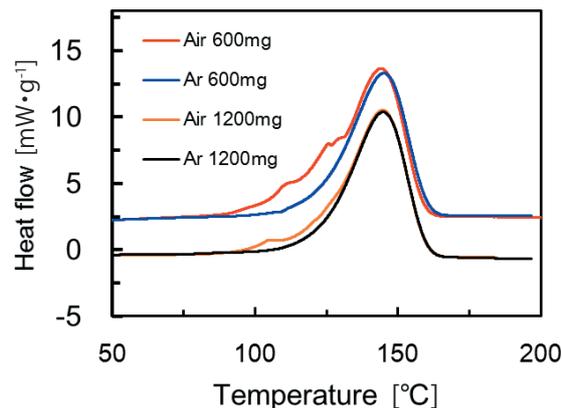


Figure 7 The heat flow curves of DTBP 10 wt% solution in air and argon measured by the C80 measurement.

obtained by the C80 was not influenced by the volume of sample.

Figure 7 shows the heat flow curves of DTBP 10 wt% solution in air and argon measured by the C80 measurement. The measurement in argon was conducted to examine the effect to DTBP decomposition with oxygen in air. The sample masses were 0.6 g and 1.2 g. The heat flow curve of C80 had the shoulder peak and the main peak. The shoulder peak observed in air was composed of multiple peaks. The shoulder peak was observed in air though it was not observed in argon.

Figure 8 shows the relationship between the sample mass of DTBP 10 wt% solution and the heat of reaction (ΔH_{intake}) in the C80 measurement. The results measured in argon was added in Figure 8. The ΔH value decreased when the sample mass increased to about 2 g. The ΔH_{intake} value became almost constant when the sample mass increased to about 5 g. This tendency was the same as the result of the DSC (Figure 4). When the free volume was larger (the sample mass was smaller), ΔH_{intake} was larger. It was presumed that ΔH_{intake} involved the heat generation in the gas phase.

The ΔH_{intake} value decreased when the sample mass was beyond 6 g. This reason of decrease of ΔH_{intake} beyond 6 g was due to the lack of oxygen in air, considering that the ΔH values in argon were almost the same as the ΔH_{intake} values of 6.10 g measured in air.

The result of Figure 8 supported the reason of the decrease of ΔH_{intake} was due to the lack of oxygen when the sample mass was more than 6 g. The ΔH_{intake} value did

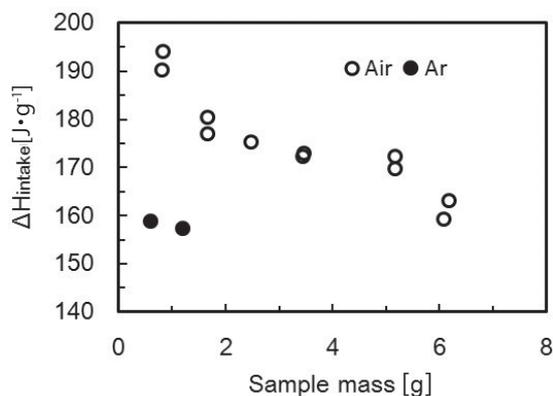


Figure 8 The relationship between the sample mass of DTBP 10 wt% solution and the heat of reaction in the C80 measurement.

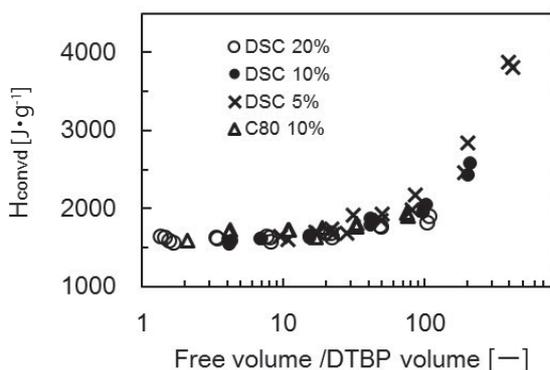


Figure 9 The relationship between the ratio of free volume to DTBP volume and ΔH_{convld} in the DSC and the C80 measurements.

not decrease from the plateau area when the sample mass increased in the result of the DSC measurement in Figure 4. It was suggested that the enough oxygen existed to react with DTBP gas in the vapor phase of the sample container in the DSC measurement. The value of 6.10 g is corresponded to 0.16 of the ratio of free volume in the C80 measurement. The minimum of the ratio of free volume was 0.22 in the case of DSC measurement.

3.3 Effect of free volume of sample container

The free volume of sample container is important value to explain the DTBP decomposition in the gas phase. Figure 9 shows the relationship between the ratio of free volume to DTBP volume and ΔH_{convld} in the DSC and the C80 measurements. DTBP volume is the value of pure DTBP. When the ratio of free volume to DTBP volume was below 20, ΔH_{convld} was almost constant.

It is desirable to measure the amount of heat with the sample mass corresponded to the range of about 20 or less ratio in order to compare the data obtained with the different container volume of the various calorimeter when DTBP solution is used as the sample. If the sample which decomposes in the gas phase is more volatile than DTBP, the ratio of free volume to the reactant is less than 20 in order to compare the data obtained with the different container volume of the various calorimeter.

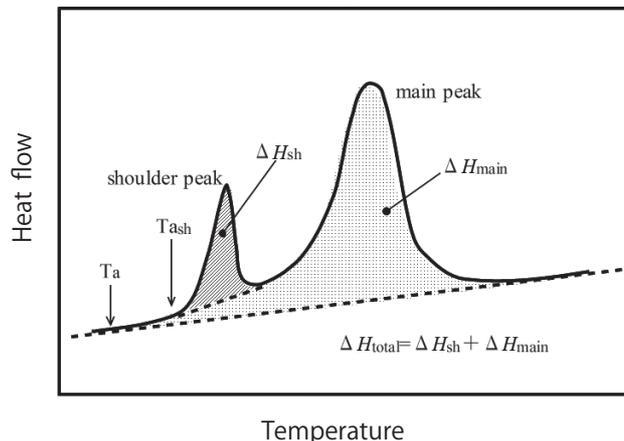


Figure 10 The schematic illustration of the measurement result of DSC and C80.

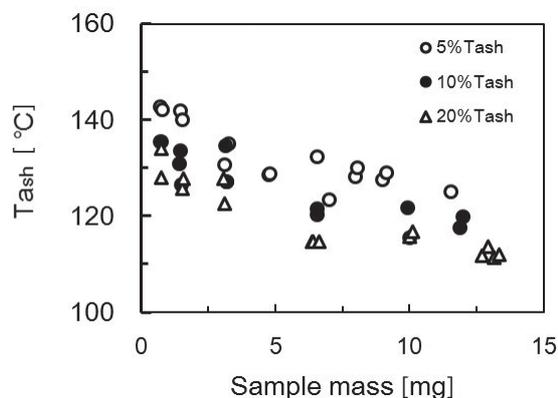


Figure 11 The relationship between the sample mass and the heat detection temperature of the shoulder peak (T_{ash}) in the DSC measurement.

3.4 Heat detection temperature

Figure 10 shows the schematic illustration of the measurement result of DSC and C80 in the DTBP decomposition. It is important to consider the heat detection temperature in the hazardous evaluation for chemical substance.

The heat generation of the main peak began at the heat detection temperature of the main peak (T_a [°C]). T_a is the temperature at which the heat flow of about 0.02 mW generated on the basis of the baseline. About 0.02 mW could be regarded as obvious heat generation.

The heat generation of the shoulder peak began at the heat detection temperature of the shoulder peak (T_{ash} [°C]). T_{ash} is the temperature at which the shoulder curve and the main peak curve intersect.

The main peak had the peak after the shoulder peak ended. The heat of reaction (ΔH_{total} [J]) is the sum of the amount of heat of the shoulder peak (ΔH_{sh} [J]) and the amount of heat the main peak (ΔH_{main} [J]).

Figure 11 shows the relationship between the sample mass and the heat detection temperature of the shoulder peak (T_{ash}) in the DSC. T_{ash} went down with an increase of the sample mass in three DTBP concentrations in Figure 10. The peak temperature of the main peak was almost constant in Figures 2 and 3 though the sample mass increased. T_{ash} of the same sample mass became higher in

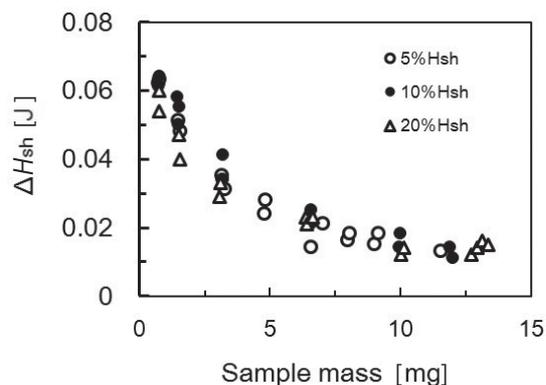


Figure 12 The relationship between the sample mass and the amount of heat the shoulder peak (ΔH_{sh}) in the DSC measurement.

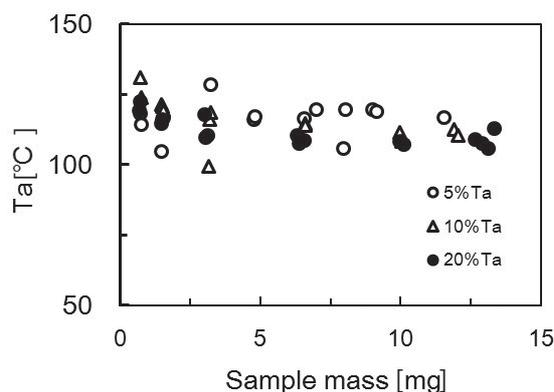


Figure 13 The relationship between the sample mass and T_a in the DSC measurement.

the order of DTBP 5 wt%, DTBP 10 wt% and DTBP 20 wt%. This tendency was remarkable regarding to samples of 7 mg or less of the sample mass.

The amount of heat is important for the hazardous evaluation for chemical substance in addition to the heat detection temperature. Figure 12 shows the relationship between the sample mass and the amount of heat of the shoulder peak (ΔH_{sh}) in the DSC. ΔH_{sh} decreased until the sample mass became about 7 mg. When the sample mass became more than about 7 mg, ΔH_{sh} became almost constant. Though the DTBP concentrations were different, the same tendency was obtained in the relationship between the sample mass and ΔH_{sh} .

When the free volume was larger (the sample mass was smaller), ΔH_{sh} was larger in Figure 12. It was presumed that ΔH_{sh} was the heat generation in the gas phase.

3.5 Reaction in liquid phase and gas phase

The heat generation of the main peak began at T_a in the liquid phase. The experimental results show the DTBP decomposition began in the gas phase after the decomposition in the liquid phase. The shoulder peak corresponded to the heat in the gas phase. The main peak corresponded to the heat in the liquid phase.

The heat generation of the shoulder peak began at T_{ash} in the gas phase. Figure 13 shows the relationship between the sample mass and T_a of DSC. T_a did not depend on the sample mass and DTBP concentration.

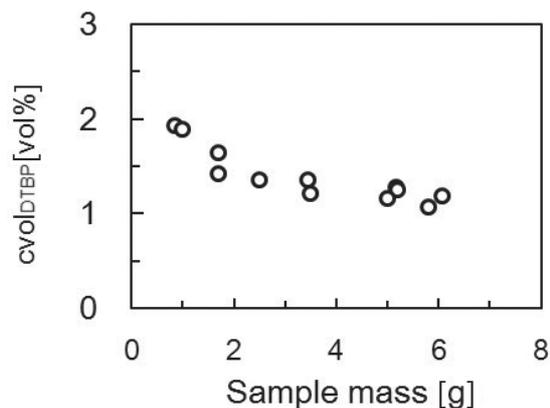


Figure 14 The relationship between the sample mass and the DTBP gas concentration in the DTBP 5 wt% measurement of the C80.

T_a of air (86.0 °C, air, 1.2 g) was almost the same as T_a of argon (81.9 °C, argon, 1.2 g) in DTBP 10wt% results of the C80 measurement (Figure 7). This result showed that the initial reaction in the liquid phase was not affected by oxygen in the DTBP decomposition.

The result of Figure 11 showed that T_{ash} of DTBP in the gas phase with low concentration DTBP solution was higher than that with high concentration. In low concentration solution, the temperature that the amount of DTBP in the gas phase reaches to certain value is considered to be higher than that in high concentration solution.

The DTBP decomposition in the gas phase was examined on the basis of the results of DTBP 5wt% by the C80. The liquid–gas phase equilibrium is presumed to realize in the sample container of the C80 measurement because the heat rate is small. If the liquid–gas phase reaches equilibrium, the DTBP mass in the gas phase can be obtained with the DTBP pressure calculated by the Antoine-type equation⁶⁾ (Equation (1)) and the Raoult's law (Equation (2)) as follows:

Antoine-type equation:

$$\log_{10}(760P) = A + B/T + C \log_{10} T + DT + ET^2 \quad (1)$$

$$\text{DTBP: } A = 17.3901, \quad B = -2.1221 \times 10^3, \quad C = 13.506, \\ D = -3.0330 \times 10^{-2}, \quad E = 1.7215 \times 10^{-5}$$

P [atm]: pure DTBP pressure, T [K]: temperature

$$W_{\text{DTBP, gas}} = \chi P V M_w / R T / 1000 \quad (2)$$

$$\text{cvol}_{\text{DTBP}} = W_{\text{DTBP, gas}} / M_w / (W_{\text{DTBP, gas}} / M_w + V / 1000 / R / 298.15) \times 100 \quad (3)$$

$W_{\text{DTBP, gas}}$ [g]: DTBP mass in the gas phase

$\text{cvol}_{\text{DTBP}}$ [%]: DTBP volume percent

V [mL]: free volume in the sample container

M_w [g·mol⁻¹]: molecular mass of DTBP (146.23)

χ [-]: molar fraction of DTBP in DTBP/toluene solution (0.032)

R [L·atm·K⁻¹·mol⁻¹]: gas constant (0.082)

Figure 14 shows the relationship between the sample mass and the DTBP gas concentration ($\text{cvol}_{\text{DTBP}}$) in the DTBP 5 wt% measurement of the C80. DTBP gas

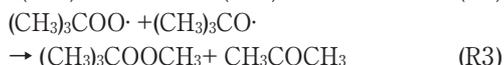
concentration was obtained on the basis of $w_{\text{DTBP, gas}}$ calculated from T_{ash} on the condition of the liquid–gas phase equilibrium. The results of Figure 14 demonstrated that the reaction started when the DTBP concentration reached to the certain gas concentration of DTBP in the sample mass of more than 2.0 g. The average value of DTBP gas concentration was 1.2 vol% in more than 2.0 g of DTBP sample mass. DTBP gas concentration was high in the range of low sample mass. It was considered as this reason that it took time for DTBP gas to occupy the free volume of C80 sample container due to large free volume and the C80 temperature rose before the liquid–gas phase equilibrium realized.

The DSC curve of DTBP 100 wt% had the shoulder peak which was the same as that of the DTBP/toluene solutions (Figure 2). The shoulder peak occurred in the gas phase and was not effect by toluene.

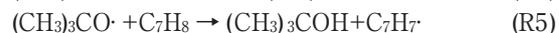
The C80 curve of DTBP 10 wt% and DTBP 100 wt%/toluene solution in argon had no shoulder peaks. DTBP did not decompose and did not react with toluene in the gas phase without oxygen.

When oxygen did not exist in the sample container, the shoulder peak (heat in the gas phase) was not observed. It was suggested that DTBP did not react with toluene in the gas phase and did not decompose in the gas phase. On the other hand, the heat was generated in the liquid phase regardless of the presence of oxygen and toluene in DTBP 100wt%.

There are several studies concerning the DTBP decomposition mechanism^{7)–9)}. The following reaction mechanisms are suggested in air on the basis of the results of these previous studies and this work. $(\text{CH}_3)_3\text{CO}\cdot$ is produced from DTBP in the gas phase ((R1)). After the oxygen directly reacts with $(\text{CH}_3)_3\text{CO}\cdot$, $(\text{CH}_3)_3\text{COO}\cdot$ is produced ((R2)). Because $(\text{CH}_3)_3\text{COO}\cdot$ is very active specie, it reacts with $(\text{CH}_3)_3\text{CO}\cdot$ and the other chemical species generating heat ((R3)).



The following reaction mechanisms are predicted in the liquid phase. $(\text{CH}_3)_3\text{CO}\cdot$ decomposes to some species generating heat in the liquid phase. $(\text{CH}_3)_3\text{CO}\cdot$ decomposes to acetone ((R4)). $(\text{CH}_3)_3\text{CO}\cdot$ reacts with toluene in the other pathway ((R5)).



4. Conclusions

DTBP/toluene solution was measured by the DSC and the C80. The heat of reaction per one gram sample decreased with an increase of the sample mass. The heat of reaction per one gram became almost constant beyond the certain sample mass in the DSC and the C80 measurements. The ratio of the free volume in the sample vessel against the sample volume is introduced to explain the behavior of this heat of reaction. The amount of heat obtained by the DSC and C80 became almost constant when the heat of DTBP/toluene solution is used as the sample.

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