

Evaluation of thermal decomposition hazards by differential adiabatic calorimeter

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Abstract

A differential adiabatic calorimeter is newly developed as the calorimeter which can estimate the thermal decomposition hazards of chemicals in the adiabatic condition that the phi-factor is equal to one. It is regarded that the adiabatic temperature rise measured by its calorimeter does not depend on the sample mass experimentally. There is a possibility that it becomes to the useful tool to estimate the hazards of the self-reactive substances. However, its propriety of the data measured by its calorimeter is not so known and familiar in the field of the hazardous evaluation of chemicals. In this report, the measurement results by its calorimeter are investigated with di-tert butylperoxide (DTBP). DTBP is one of the self-reactive substances and used as standard sample of the ARC. Activation energy of DTBP in the thermal decomposition is obtained and is compared with the literature value. The property of DTBP decomposition is investigated by the measurements data. In addition, its calorimeter is applied to the evaluation of the thermal decomposition hazards of the other self-reactive substance. N, N'-dinitroso pentamethylene tetramine (DPT) is one of the blowing agents which is high reactive material. DPT became the cause material of some fire accidents in the past. In this report, the heat onset temperature and the activation energy of DPT are measured in the adiabatic condition. The decomposition reaction is discussed on the basis of the measurements data.

Keywords : differential adiabatic calorimeter, thermal decomposition, di-tert butylperoxide, N, N'-dinitroso pentamethylene tetramine

1. Introduction

A differential adiabatic calorimeter (DAC) had been developed to obtain the thermokinetic data during runaway reactions on the adiabatic condition. The adiabatic condition means heat losses to the surroundings are avoided. There are some adiabatic equipments for the evaluation for the thermal decomposition hazards. The adiabatic calorimeter can provide data for evaluating potential hazards of reactive chemicals. The phi-factor is important value on the adiabatic investigation using the adiabatic calorimeters. The phi-factor represents heat that is used to heat up the sample container. All of the heat release which occurs from the sample during the thermal decomposition is used to heat up only sample when the phi-factor is one. The accurate evaluation for the thermal decomposition hazards regarding to the large amount of sample become possible on the condition that the phi-

factor is near one. The adiabatic calorimeter with a large-scale sample mass and low thermal inertia give useful data near the real condition on the storage, its handling and transportation of the sample.

The DAC can realize the adiabatic measurements on the condition that the phi-factor equals to one. The DAC gives the sample heat which is supposed to heat up the sample container with the reference container and the compensation heaters for the sample container and the reference container. The DAC is an extremely useful tool for assessing thermal hazards of reactive chemicals. The data obtained by the DAC is important information for the design of the safe industrial process.

However, the DAC is not so familiar in the field of the chemical reactivity evaluation. In this report, the measurement results by the DAC are studied with di-tert butylperoxide (DTBP). DTBP is one of the self-reactive

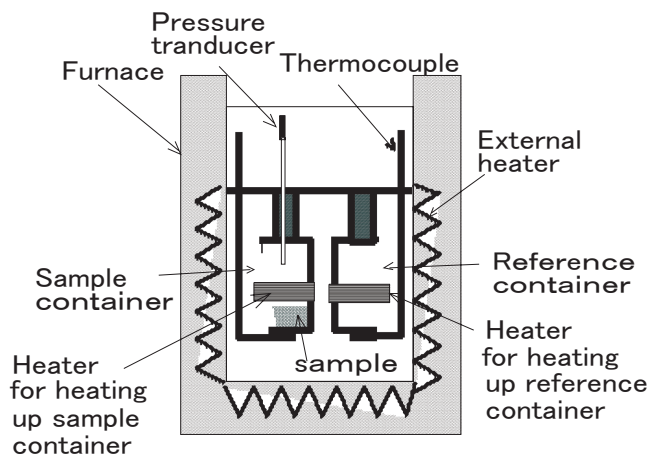


Figure 1 Schematic of differential adiabatic calorimeter.

substances and used as standard sample of the ARC (accelerating rate calorimeter), RSST (reaction system screening tool) and the APTAC (auto pressure tracking adiabatic calorimeter¹⁾⁻⁵). The apparatus properties and the reliability of the data obtained by the DAC were examined on the basis of the measurement data of various concentrations and mass of DTBP/toluene solution. The thermodynamic parameters such as the heat of reaction and the activation energy in the thermal decomposition obtained by the DAC were compared with the literature values. The thermal decomposition of DTBP/toluene solution was studied by the data measured with the DAC.

In addition, the DAC was applied for the evaluation of the thermal decomposition hazards of the other self-reactive substance. N, N'-dinitroso pentamethylene tetramine (DPT) is one of the blowing agents which is high reactive material⁶). DPT became the cause material of some fire accidents in the past. In this report, the heat onset temperature and the activation energy of DPT were measured and investigated in the adiabatic on the condition that the phi-factor nearly equals to one.

2. Experimental

2.1 Apparatus

A schematic of the DAC is shown in Figure 1. The sample and the reference containers are used in the DAC. Both of container volumes are 9 mL approximately. The thermocouples are used to measure the temperature of both of container walls. The adiabatic control is conducted with the external heater and thermocouples for the sample and reference container.

The DAC supplies heat that is need for heating up the sample container by the compensation heater for the sample container when the sample generates heat. At the same time, heat is supplied for the reference container by the compensation heater for the reference container.

2.2 Samples

All experiments were performed in a closed container with the ambient air. DTBP/toluene solutions with various mass and concentration were used in experiments. The duplicate tests were conducted. The concentration range of DTBP was between 10wt% and 30wt% in toluene

solutions. DTBP 15wt%/toluene solution is the standard sample in the adiabatic investigation. The sample mass of DTBP/toluene solution used in the tests were 1.0 g, 3.0 g, 5.0 g and 8.0 g. Pure DPT was used as the sample. The sample mass of DPT is 0.050 g, 0.10 g, 0.15 g and 0.30 g.

2.3 Measurement conditions

The threshold to detect an exothermic reaction is 0.01 Kmin⁻¹ of the heat rate. The maximum value of heat rate supplied by the DAC is 100Kmin⁻¹ approximately. The sample temperature is automatically incremented by 5K in the case that the exotherm more than 0.01Kmin⁻¹ is not detected by the thermocouple of sample container wall. The shutdown criterion of heat rate is not set in the DAC. The pressure is expressed by the gage pressure.

2.4 Heat of reaction

The heat of reaction per one gram of the sample (ΔH in J/g-intake) is obtained by the following equation regarding to the DAC.

$$\Delta H (\text{J/g-intake}) = C_s \Delta T_{ad} \quad (1)$$

The adiabatic temperature rise (ΔT_{ad} in K) equals ($T_{max} - T_0$). T_0 (K) and T_{max} (K) mean the heat onset temperature and the maximum temperature, respectively. C_s ($\text{Jg}^{-1}\text{K}^{-1}$) value is the sample specific heat averaged by each temperature closed to T_0 and T_{max} ($2.1 - 2.3 \text{Jg}^{-1}\text{K}^{-1}$). Though the phi-factor (ϕ) is one in the DAC, it is defined commonly in the adiabatic investigation as:

$$\phi = 1 + (McC_c) / MsC_s \quad (2)$$

ϕ is the phi-factor. Mc (g) is the sample container mass, Ms (g) sample mass, C_c ($\text{Jg}^{-1}\text{K}^{-1}$) the sample container specific heat. The C_c value is the specific heats averaged by each temperature closed to T_0 and T_{max} .

ΔH (J/g-intake) is calculated by the following equation in the common adiabatic investigation.

$$\Delta H (\text{J/g-intake}) = \phi C_s \Delta T_{ad} \quad (3)$$

2.5 Decomposition kinetics

The sample temperature (T in K) and T_{max} are measured experimentally. When the reaction order is one, k is expressed by the following the equation:

$$k = (dT/dt) / (T_{max} - T) \quad (\text{reaction order}=1) \quad (4)$$

The activation energy and the frequency factor are expressed by the following equation:

$$\log k = \log(A) - (1/2.303) (E/R^1 T^{-1}) \quad (5)$$

E is the activation energy (Jmol^{-1}), k rate constant (s^{-1}), and A is the frequency factor (s^{-1}). R is the gas constant ($8.314 \text{Jmol}^{-1}\text{K}^{-1}$). E and A are obtained by $\log k$ versus T^{-1} plot. E is the slope and A is the intercept on the straight line.

3. Results and discussion

3.1 DTBP

Figure 2 and 3 show the heat rate and the pressure rate in the same measurement. The sample was 5.0 g of DTBP

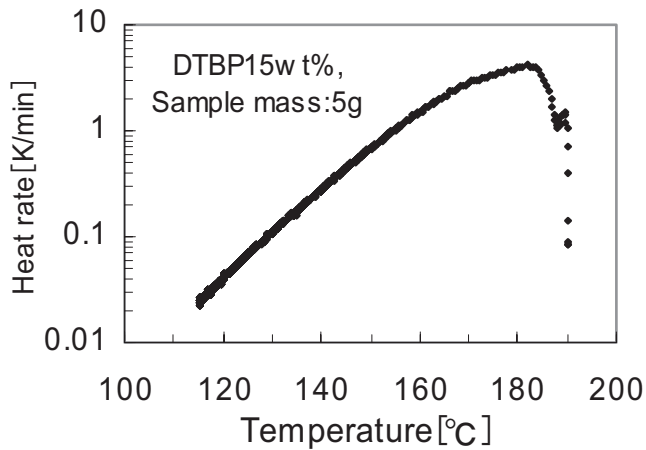


Figure 2 Relationship between temperature and heat rate.

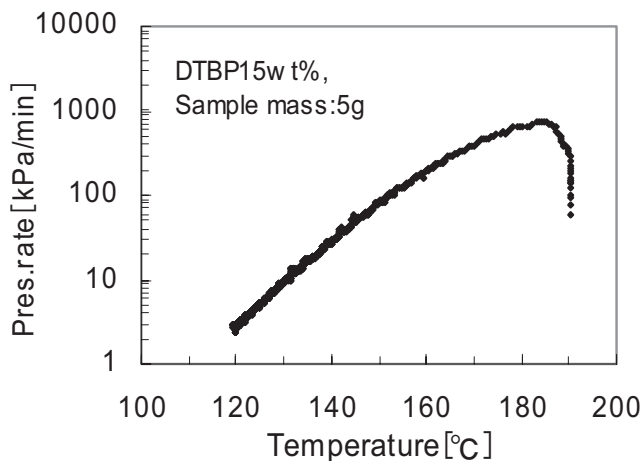


Figure 3 Relationship between temperature and pressure rate.

15wt%. DTBP15wt% is used for the standard sample of the adiabatic test¹⁾. The averaged heat onset temperature was 115°C. The averaged maximum temperature and the averaged maximum pressure were 190°C and 10.7 MPa. The averaged maximum heat rate and the averaged maximum pressure rate maximum were 3.65 Kmin⁻¹ and 687 kPa·min⁻¹.

The relationship between the mass of DTBP 15wt% and the heat of reaction (ΔH in J/g-intake) is shown in Figure 4. ΔH is the value per one gram of sample. It was suggested the correct adiabatic temperature rise could not be obtained when the sample mass was less than 5.0 g of DTBP15wt%. There was the possibility that the threshold to detect an exothermic reaction of DAC because the occurred heat from the sample was not conducted to the thermocouple when it was small. The averaged value of the heat of reaction was 189 J/g-intake of 8.0 g. The heat of reaction of DTBP15wt% of less than 5.0 g was not enough for heating up the sample container. The ΔH of DTBP15wt% by measured by the ARC was 212 (J/g-intake). Both of ΔH of DAC and that of ARC were similar when the sample mass of 8.0 g was used. The maximum heat rate (HR_{\max} in Kmin⁻¹) was added to Figure 4. HR_{\max} increased when the sample mass increased.

T_0 , T_{\max} , ΔH , HR_{\max} , the maximum pressure (P_{\max} in

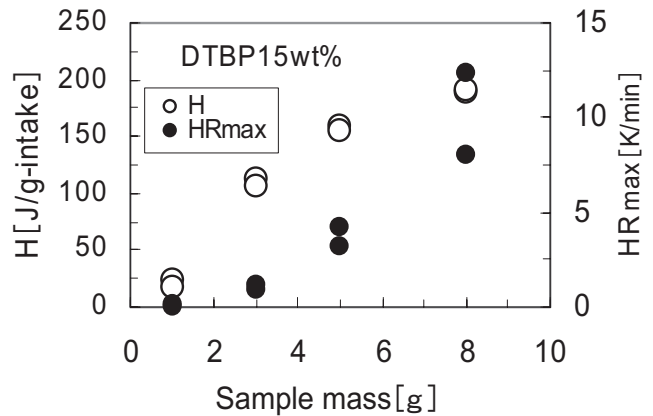


Figure 4 Relationship between mass of DTBP15wt% and heat of reaction.

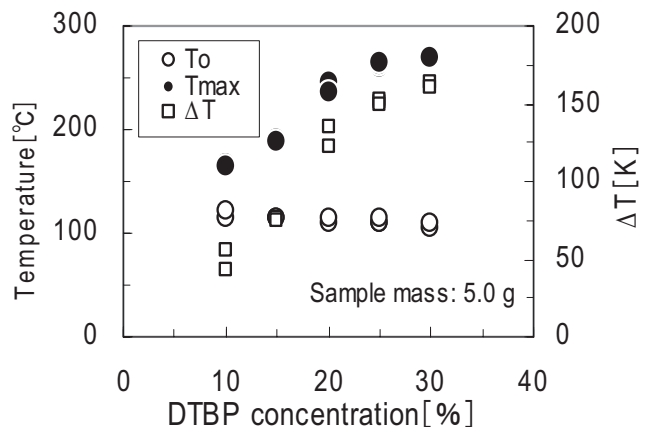


Figure 5 Relationship between DTBP concentration and T_0 , T_{\max} , ΔT .

kPa) and the maximum pressure rate (PR_{\max} in kPa·min⁻¹) for the DTBP concentration were investigated when the sample mass of DTBP/toluene solution was more than 5.0 g. The concentration range was from 10wt% to 30wt%. The relationship between the DTBP concentration and T_0 , T_{\max} in the addition to ΔT_{ad} are shown in Figure 5. T_0 decreased when the DTBP concentration increased. T_0 of DTBP15wt% of 8.0 g was 110°C. This value was lower than that of the ARC (117°C). One of reasons was that the threshold to detect an exothermic reaction of DAC (0.01 Kmin⁻¹) was lower than that of ARC (0.02 Kmin⁻¹). T_{\max} increased when the DTBP concentration increased. The slope of T_{\max} for the DTBP concentration was larger than that of T_0 . The increase of T_{\max} effect the increase of ΔT_{ad} strongly compared with the decrease of T_0 when the DTBP concentration increased. The increased of ΔT_{ad} led to the increase of ΔH when the DTBP concentration increased.

The relationship between the DTBP concentration and ΔH is shown in Figure 6. ΔH is the value per one gram of sample. The straight line was obtained from DTBP 10wt% to DTBP 25wt%. The straight line obtained from DTBP 10wt% to DTBP 25wt% did not pass on the origin of the coordinate axes. There was the possibility that the reaction mechanism of DTBP with toluene changed around 10wt% of DTBP concentration. The heat of

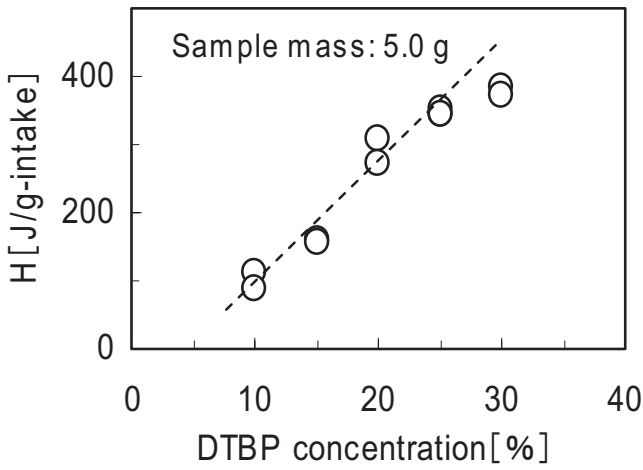


Figure 6 Relationship between DTBP concentration and heat of reaction.

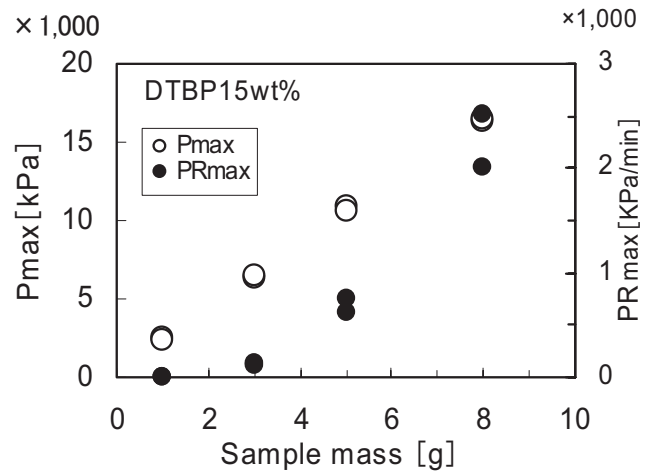


Figure 8 Relationship between sample mass and maximum pressure, maximum pressure rate.

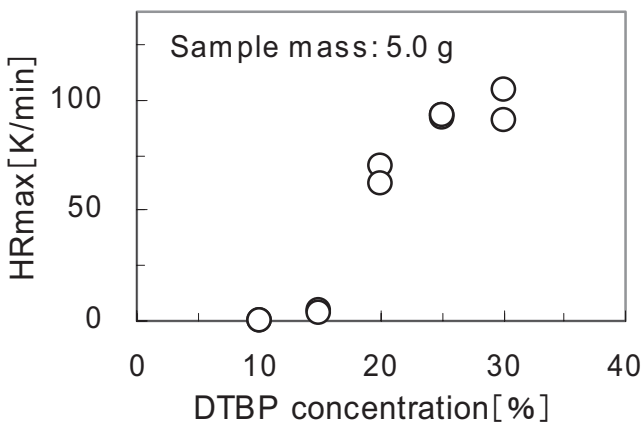


Figure 7 Relationship between DTBP concentration and maximum heat rate.

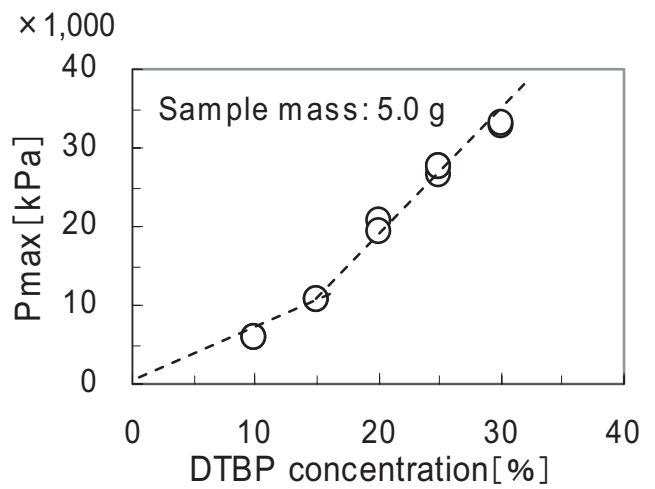


Figure 9 Relationship between DTBP concentration and maximum pressure.

reaction of DTBP30wt% did not pass on the straight line. It meant the external heater for the adiabatic control did not work correctly because the heat of reaction of DTBP 30wt% was large.

Figure 7 shows the relationship between the DTBP concentration and HR_{max}. HR_{max} increased when the DTBP concentration increased. HR_{max} increased rapidly beyond 15wt% of DTBP concentration. HR_{max} of DTBP 30wt% increased because HR_{max} of DTBP 30wt% (about 100 Kmin⁻¹) was the limit of the adiabatic control of the DAC.

The relationship between the mass of DTBP15wt%/toluene solution and P_{max} in addition to PR_{max} is shown in Figure 11. P_{max} increased proportionally when the DTBP concentration. The decomposition gas occurred when DTBP decomposed in toluene. It demonstrated that the amount of gas was in proportional to the amount of DTBP in toluene. It showed the pressure measured by the DAC was appropriate and correct. PR_{max} increased exponentially for the increase of the mass of DTBP 15wt%. PR_{max} meant the intensity of decomposition. The relationship between the DTBP concentration and P_{max} is shown in Figure 9. P_{max} increased when the DTBP concentration increased. The increase rate of P_{max} for the concentration became larger than the proportional increase rate for the concentration near DTBP 15wt%. It implied DTBP reacted with toluene on the basis of the

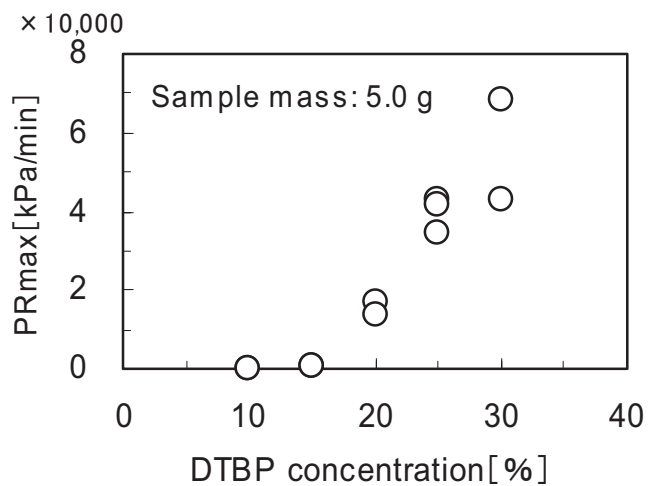


Figure 10 Relationship between DTBP concentration and maximum pressure rate.

results of P_{max} for the increase of the mass and the concentration of DTBP. If DTBP did not react with toluene, the proportional relationship would be obtained in P_{max} vs. DTBP concentration diagram. The relationship between the DTBP concentration and PR_{max} is shown in Figure 10. PR_{max} increased exponentially when the DTBP

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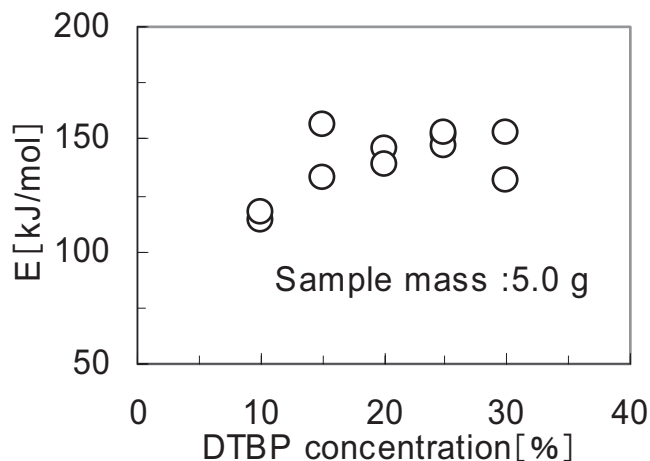


Figure 11 Relationship between DTBP concentration and activation energy.

concentration increased. PR_{max} did not saturate though there was the tendency that HR_{max} saturated in DTBP 30 wt% in Figure 7. The increase HR_{max} and PR_{max} for the DTBP concentration at given mass of DTBP could be predicted on the condition that the phi-factor was one on the basis of the results of Figures 7 and 10.

The HR and PR data that phi-factor was nearly one could be measured with 5.0 g of DTBP 15wt%. The activation energy (E in kJmol^{-1}) was calculated with the slope of the straight line in $\log k$ vs. T^{-1} . The kinetic plot in the decomposition of DTBP/toluene solution showed the reaction number could be regarded as the first-order of the overall reaction in all of the concentrations because the fitting curve was straight. The relationship between the DTBP concentration and the activation energy is shown in Figure 11. The activation energy was almost the constant for the DTBP concentration range from 10wt% to 30wt%. This result showed the reaction process did not vary largely in the different DTBP concentrations. The averaged E of DTBP 15wt% was 151 kJ/mol when the samples of 5.0 g and 8.0 g were used. The activation energy was smaller than the literature value (157.3 kJmol^{-1}). There was possibility that the DAC calculated E on the basis of the heat rate with the slow temperature rise of the lower temperature range than that of the ARC.

3.2 DPT

Figure 12 shows the time profile of the heat rate in DPT decomposition. The sample mass of DPT was 0.15 g. The heat of reaction could not be measured because the heat rate saturated. DPT decomposition had three steps when the samples of 0.050, 0.10 and 0.15 g. The activation energy of the first step and the second step were 65.6 kJ/mol and 253 kJ/mol in the sample mass of 0.15 g. The range of the first step was from 125–150°C. The range of the second step was from 150–170°C. DPT of 0.30 g had one step decomposition with E of 127 kJmol^{-1} . The averaged E of the second step was 253 kJmol^{-1} which was similar to the literature measured by the APTAC (215 kJmol^{-1}). The sample mass was from 0.10 to 0.13 g in the APTAC measurements. When the amount of DPT increased beyond 0.15 g, the decomposition mechanism could vary.

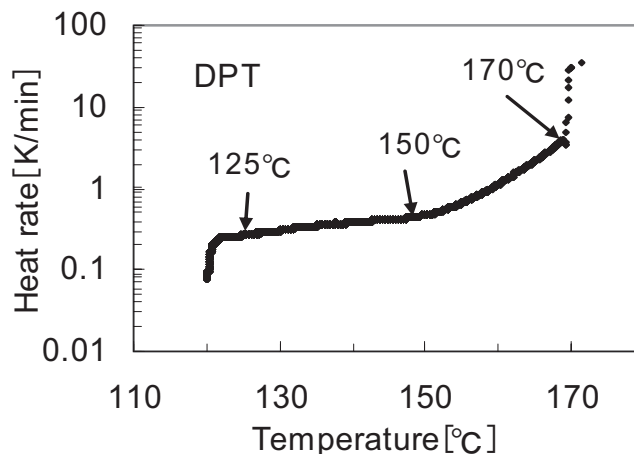


Figure 12 Relationship between temperature and heat rate.

4. Conclusions

The properties and the reliability of the differential adiabatic calorimeter (DAC) were investigated with DTBP/toluene solution. The thermal decomposition of DTBP and DPT was studied on the basis of the data of DAC. The following conclusions were obtained.

- (1) The heat of reaction measured by the DAC became lower than the literature value. The activation energy was almost the constant for DTBP concentration by the DAC. The activation energy obtained by the DAC was lower than the literature value obtained by the ARC.
- (2) More than 5.0 g of sample mass was needed to obtain the appropriate data with the DAC. The heat rate and the pressure rate data that phi-factor was nearly one could be measured with 5.0 g of DTBP15wt%.
- (3) It was suggested the reaction mechanism changed near DTBP15wt% of DTBP in toluene on the basis of results of the maximum pressure for the DTBP concentration.
- (4) DPT decomposition had three steps when the samples of less than 0.15 g. The averaged E of the second step was similar to the literature value measured by the adiabatic calorimeter. When the amount of DPT increased beyond 0.15 g, the decomposition mechanism could vary.

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示差断熱型熱量計を用いた熱分解の危険性評価

岩田雄策*†

示差断熱型熱量計 (DAC) は試料容器の熱慣性を補正することによって補正を行わずに発熱速度等のデータを取得できる特徴がある。しかし、本装置を用いた測定データ及び研究例が少なく、本研究において、本装置の信頼性に対する検証取得データの検証を行った。断熱型熱量計の標準物質として使用されるDTBPを試料として用いた。また、DACの測定データを用いてDTBP (di-tert butylperoxide) の熱分解反応についても考察を行った。さらに火災事例が多くみられる自己反応性物質であるDPT (N, N'-dinitroso pentamethylene tetramine) にDACを適用した。その結果、DTBPはトルエンと反応し、15%-20%で反応形式が変化することが明らかになった。DACの測定データについて、他の断熱型熱量計 (ARC等) による文献値と比較すると試料量が5 g以上であれば信頼性のあるデータが取得できた。この理由としては試料容器の熱慣性を完全に補正できないことが挙げられる。また、DPTの反応は3段階で最後の反応は非常に急激であることが分かった。

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