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THERMAL RISK EVALUATION OF ORGANIC PEROXIDE BY AUTOMATIC PRESSURE TRACKING ADIABATIC CALORIMETER

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An automatic pressure tracking adiabatic calorimeter (APTAC) has been developed to obtain the thermokinetic and vapor pressure data during runaway reactions. The heat onset temperature is important data for estimating the thermal hazardous materials. DTBP(di-*tert*-butyl peroxide)/toluene was chosen for evaluating the measurement values and the thermokinetic parameters. The relationships between the sample mass and the heat onset temperature in the addition to the maximum temperature were investigated to explain the heat of reaction measured by the APTAC. The apparatus properties and the reliability of the data obtained by the APTAC were examined on the basis of the experimental data.

Keywords: *automatic pressure tracking adiabatic calorimeter, di-tert-butyl peroxide, heat of reaction, heat onset temperature, thermal decomposition*

Introduction

An APTAC is the adiabatic calorimeter which can provide data for evaluating potential hazards of reactive chemicals. The APTAC can also track pressure rise of the sample inside the sample vessel. The data obtained by the APTAC is the important information for evaluating the heat release and the heat onset temperature to design the safe industrial process. The measurement results are useful for safety storage, handling and transportation of chemicals.

The ARC is one of the popular adiabatic calorimeters in the hazardous evaluation methods of the self-reactive substances. The principle of the adiabatic system of the APTAC is the same as the accelerating rate calorimeter (ARC) [1]. The properties of the APTAC are the adiabatic calorimeter with the large-scale sample mass and the low thermal inertia [2]. The pressure is generated outside the sample vessel to cancel the pressure difference during a reaction. The glass sample vessel can be used to prevent the catalytic effect by the surface of the metal sample vessel.

However, the APTAC is not so widely used in the field of the chemical reactivity evaluation. Therefore the properties of the data obtained by the APTAC have not been so familiar. The DTBP(di-*tert*-butyl peroxide) /toluene was chosen for evaluating the measurement values and the thermokinetic parameters. DTBP/toluene solution was used to evaluate the properties of the ARC measurements [3, 4]. The apparatus properties and the reliability of the data obtained by the APTAC are examined on the basis of the experimental data of the heat onset temperature, the maximum temperature and the heat of reaction.

Experimental

Samples

All experiments with the APTAC were performed in a closed vessel environment with the ambient air above the sample. DTBP/toluene solutions were used to examine the properties of the data obtained by the APTAC. DTBP had been used to confirm the properties and the reliabilities of the ARC data. The range of DTBP concentrations was between 20 and 60% in toluene solutions. Sample masses of DTBP/toluene solution were between 3 and 40 g. The range of the φ-factors was between 1.8 and 9.1.

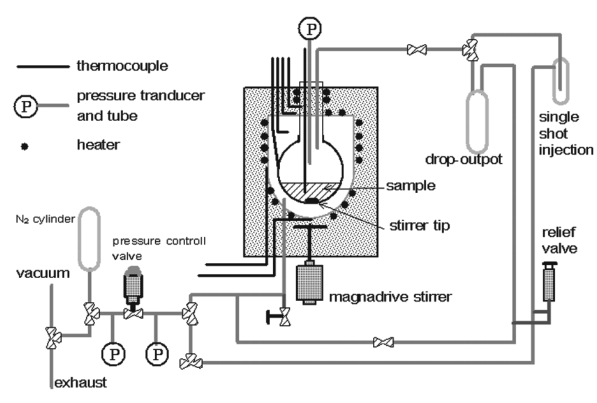

Fig. 1 Outline of the APTAC apparatus

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The heat of reaction of DTBP 100% and DTBP 38% was measured with the closed stainless steel cells by the DSC (differential scanning calorimeter). The heating rate was 10 K min^{-1}. The sample masses were between 1.6 and 2.4 mg in the DSC experiments.

Apparatus

A schematic of the APTAC calorimeter is shown in Fig. 1. Three-type N thermocouples are used to measure the temperature inside the sample, the surface temperature of the sample vessel wall and the ambient temperature. The spherical sample vessel is screwed at the top heater and the sample thermocouple passes directly into the sample vessel through a fitting on the top heater. The APTAC maintains a sample in an adiabatic condition once an exothermic reaction is detected. The top, side, bottom and tube heaters are used to control the temperature inside the sample adiabatically. The adiabatic condition is maintained by the temperature control so that the sample and the ambient temperatures exactly equal. Because the pressure of the outside of the sample vessel is controlled to equal to the pressure inside the sample vessel which is changed by the reaction, the glass vessels such as made of weak materials or the sample vessels with the low thermal inertia of a large- scale mass can be used in the experiments. The φ-factor indicates the thermal inertia. The φ-factor is close to one when the sample mass is large. The φ-factor is defined as:

$$\varphi=1+(M_c C_c)/(M_s C_s) \qquad (1)$$

M_c (g) is the sample vessel mass, M_s (g) is the sample mass, C_c (Jg^{-1} K^{-1}) is the sample vessel specific heat, and C_s (Jg^{-1} K^{-1}) is the sample specific heat. The C_c and C_s values are the specific heats averaged by each temperature close to the heat onset temperature and the maximum temperature. The data of the specific heat are obtained in the literature [5].

DSC was used to measure the heat of reaction of DTBP 100% and DTBP 38% toluene solution.

Measurement conditions

Volume of the glass sample vessel is 130 cm^3. The borosilicate glass sample vessels are used in the measurement of DTBP/toluene solutions. The glass vessel is used to prevent the catalytic effect of the metal vessel surface in the experiments. The thermocouple for the temperature measurement inside the sample is covered with a Teflon tube. The threshold to detect an exothermic reaction is 0.05 K min^{-1} of the heat rate. The sample temperature was automatically incremented by 10 K in the case that the exotherm more than 0.05 K min^{-1} is not detected by the thermocouple inside sample. The shut down criteria of heat rate is 400 K min^{-1}. Reactions can be followed up to about 400 K min^{-1}. The shut down condition depends on the heating ability by the heaters of the APTAC. Pressure rise inside the sample vessels during the reactions are followed up to about 7 500 kPa of the pressure and 75 000 kPa min^{-1} of the pressure rate.

Results and discussion

Example of measurement

The experiments were conducted using DTBP/toluene solution to investigate the properties of the APTAC. The measurement results by the APTAC were used to investigate the DTBP decomposition. The APTAC detects the sample temperature directly and controls the adiabatic conditions by the sample temperature. Figure 2 shows an example of the heat rate and the pressure rate of DTBP 50%/toluene solution. The sample mass is 9.2 g (φ=3.8). The maximum heat rate is 282 K min^{-1}.

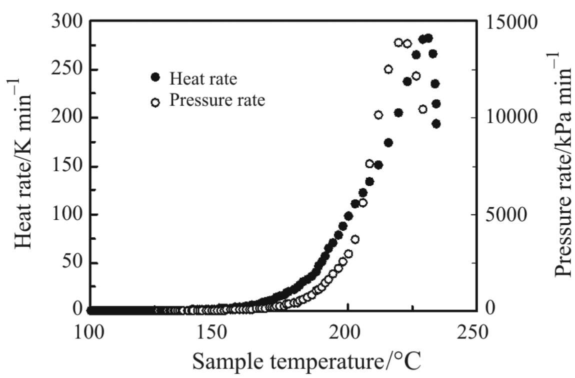

Fig. 2 Heat rate and pressure rate measured by APTAC. Sample is DTBP 50%/toluene solution. Sample mass is 9.2 g (φ=3.8)

Heat onset temperature

It is confirmed that a reaction can be followed adiabatically up to at least 400 K min^{-1} on the basis of the heat rate data of DTBP/toluene solution with various masses and concentrations in the previous paper [6]. The heat rate increases with the increase of the DTBP mass in toluene exponentially in various DTBP concentrations.

The relationship between the sample mass and the heat onset temperature (T_o) with various concentrations is shown in Fig 3. These T_o values are the average value of some tests results. The heat onset temperatures of various sample masses are in the temper-

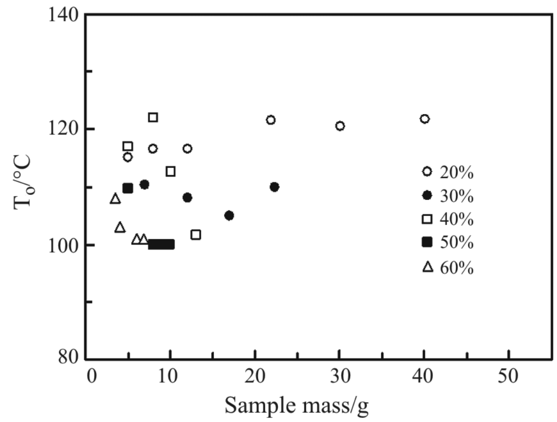

Fig. 3 The relationship between sample mass and the heat onset temperature with various sample masses

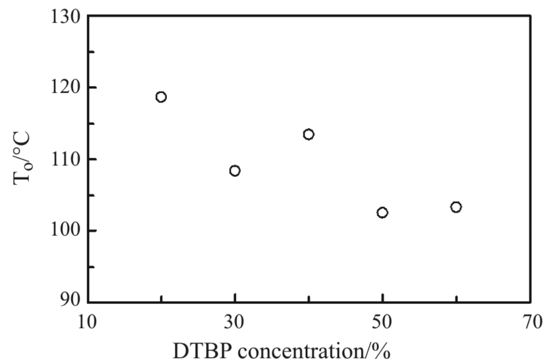

Fig. 4 Relationship between DTBP concentration and heat onset temperature averaged on various sample masses

ature range of 10 K approximately excluding the heat onset temperatures of DTBP 40%.

Figure 4 shows the relationship between the DTBP concentration and T_o averaged on various sample masses. The averaged T_o decreases with the increase of DTBP concentration. The T_o value is nearly constant in more than 50% of concentration.

The sample temperature and the vessel wall temperature are measured by the APTAC. The adiabatic control of the APTAC is conducted not by the vessel wall temperature, but by the sample temperature. In contrast, the adiabatic control of the ARC is conducted by the vessel wall temperature. There is the possibility that the APTAC can measure the sample temperature rise with high sensitively, compared to the ARC though the exotherm threshold of ARC (0.02 K min^{-1}) is lower than that of the APTAC (0.05 K min^{-1}) in this work.

The heat of reaction is one of the important kinetic parameters to evaluate the thermal hazard of the self-reactive substances. The heat of reaction is calculated by Eq. (2) on the basis of the data obtained by the APTAC [7] :

$$\Delta H = 100\ \varphi\ (T_{max} - T_o)\ C_s M_w / x \qquad (2)$$

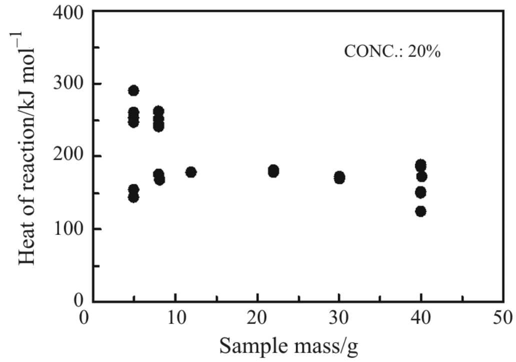

Fig. 5 Heat of reaction *vs.* various sample masses of DTBP20%

where ΔH (J mol^{-1}) is the heat of reaction, M_w (g mol^{-1}) is the molecular mass of DTBP (146.22) and x (%) is the mass percent of DTBP in toluene. When the φ-factor is calculated, C_c and C_s are the specific heat averaged between the near heat onset temperature and the near maximum temperature. The ΔH value of Eq. (2), which is measured using the APTAC data, is obtained in the same way as the ARC. This equation is originally used in order to obtain the heat of reaction on the basis of the T_{max} and T_o values measured by the ARC.

The heat of reaction for various sample masses of DTBP 20% is shown in Fig. 5. The values of the heat of reaction are converted to that of DTBP 100%. The deviation in the heat of reaction is large in the samples of 5.0 and 8.0 g, compared to samples of the other mass. There is a cause in the deviation of the heat onset temperature of the sample with the small mass. It is difficult for the APTAC to search an exotherm because the heat release from the sample with the small mass of 20%. is small. The deviation range in the heat onset temperature of 5.0 and 8.0 g is 10 K approximately. The sample masses of 5.0 and 8.0 g are corresponded to 7.6 and 5.1 of the large φ-factor. When the heat of reaction is calculated, the deviation of ($T_{max} - T_o$) expands because of the large φ-factor.

The relationship between the DTBP concentration and the heat of reaction measured by the APTAC is shown in Fig. 6. The heat of reaction values are in pure form of DTBP. The heats of reaction of DTBP 20% with 5.0 and 8.0 g were excluded. When the samples with the high concentration were used, the large amount of sample could not be measured because the heat rate exceeded 400 K min^{-1}. When the heat of reaction is calculated, the deviation of (T_{max}–T_o) expands because of the large φ-factor.

The heat of reaction of DTBP 25% measured by the APTAC in the literature was 197.7 kJ mol^{-1} [2]. This value is in good agreement with that of DTBP 30% in this work. This result shows our mea-

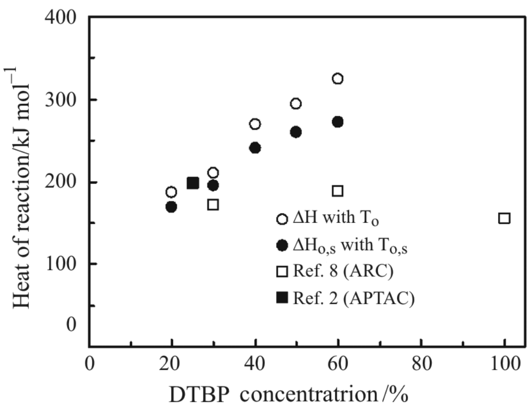

Fig. 6 Relationship between DTBP concentration and heat of reaction corrected in heat onset temperature

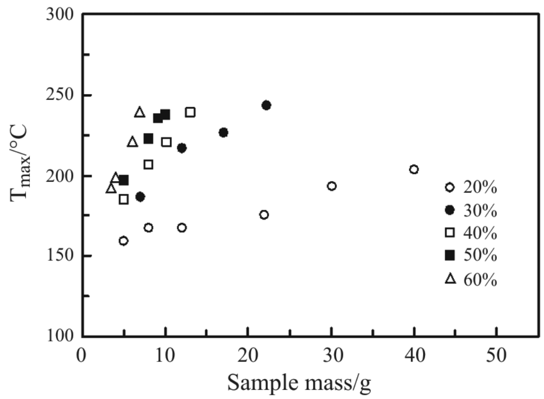

Fig. 7 Relationship between sample mass and maximum temperature with various sample masses

surements of the APTAC are appropriate. The heats of reaction of DTBP 30%, DTBP 60% and DTBP 100% measured by the ARC are 171.6 kJ mol^{-1}, 188.4 and 154.9 kJ mol^{-1}, respectively [8]. The ΔH values obtained by the APTAC are larger than those of the ARC. The difference between the ΔH value of APTAC and the ΔH value of the ARC is larger in the high concentration of DTBP 60%. This is because there is the possibility that T_o measured by the APTAC is lower than that of the ARC. The heat onset temperature by the APTAC is the temperature inside the sample. In contrast, the heat onset temperature by the ARC is the wall temperature of the sample vessel. The heat of reaction obtained by the APTAC should be corrected because Eq. (2) assumes the temperature data of the vessel wall such as the ARC. The corrected heat onset temperature ($T_{o,s}$) should be introduced on the basis on the measured T_o to evaluate the heat of reaction. The corrections of the heat onset temperature and the heat of reaction are described as follows [9]:

$$1/T_{o,s}=1/T_o-(R/E)\ln\varphi \qquad (3)$$

$$\Delta H_{o,s}=100\varphi(T_{max}-T_{o,s})C_sM_s/x \qquad (4)$$

where T_{max} (K) is the measured maximum temperature by the APTAC, T_o (K) is the measured heat onset temperature by the APTAC, $T_{o,s}$ (K) is the corrected heat onset temperature, E (J mol^{-1}) is the activation energy, R (J mol^{-1} K^{-1}) is the gas constant (8.314) and $\Delta H_{o,s}$ (J mol^{-1}) is the corrected heat of reaction obtained using the corrected heat onset temperature.

The E value is calculated from the reciprocal of the sample temperature–logarithm of the rate constant plot. The E and log(A, 1/s) values of DTBP 30% obtained by the ARC in the literature were close to the values obtained by the APTAC [6]. It is elucidated that the experimental method with the APTAC and the data analysis are appropriate in the measurement of the APTAC. In addition, this result shows the decomposition mechanism in the ARC is the same as that in the APTAC.

$T_{o,s}$ is the corrected value converted to the temperature at the wall of the sample vessel. The relationship between the DTBP concentration and the heat of reaction obtained with T_o and $T_{o,s}$ is shown in Fig. 6. Figure 6 expresses $\Delta H_{o,s}$ becomes close to the literature values though the difference between ΔH and $\Delta H_{o,s}$ become larger with the increase of the DTBP concentration.

Maximum temperature

The APTAC can obtain the value close to the maximum temperature of sample in the condition that the φ-factor is one because it measures the sample temperature directly. The maximum temperature of the APTAC is useful for evaluating the thermal hazards of chemical substances.

The relationship between the sample mass and the T_{max} value with various concentrations is shown in Fig. 7. These T_{max} values are the average values of some tests results. The T_{max} value of the high DTBP concentration is higher than that of the low DTBP concentration when the sample mass is the same. The T_{max} value increases with the increase of the sample mass in all concentrations while the T_o value is nearly constant for the sample mass. It indicates the φ-factor have the effect on the T_{max} value though the adiabatic condition is controlled by the sample temperature.

There is the discrepancy between $\Delta H_{o,s}$ and the heat of reaction obtained by the ARC. It is necessary to make more correction for $\Delta H_{o,s}$ value to become close to the heat of reaction obtained by the ARC. The T_{max} value should be corrected because it is the temperature inside the sample of the APTAC. The T_{max} value of the sample temperature is commonly higher than the vessel wall temperature when the reaction

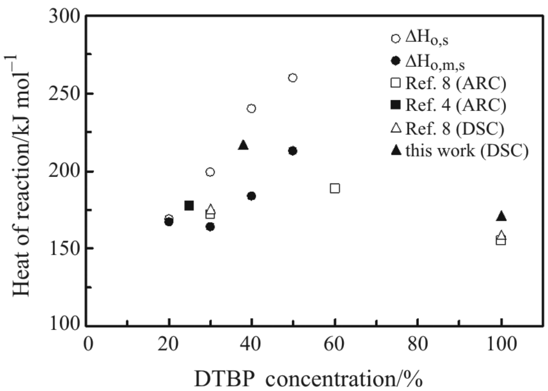

Fig. 8 Relationship between DTBP concentration and heat of reaction corrected in maximum temperature in addition to heat onset temperature

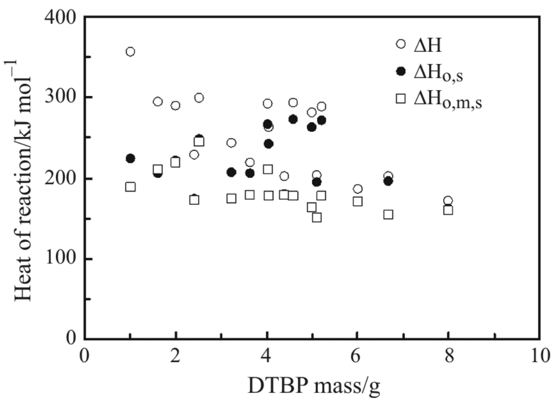

Fig. 9 Relationship between DTBP mass in toluene and corrected heat of reaction

occurs near the sample thermocouple. However, the vessel wall temperature was higher than the sample temperature when some of DTBP20% samples of 30 and 40 g were measured. It indicates the reaction occurs near the vessel wall the some cases that the large amount of sample is used.

The T_{max} value is measured by the thermocouple inside the sample in the APTAC while the part of the generated heat conducts to the wall of the sample vessel. The vessel wall temperature increases following the sample temperature except some of DTBP 20% samples of 30 and 40 g in the APTAC experiments. The T_{max} value is commonly higher than the vessel wall temperature. The vessel wall temperature at T_{max} ($T_{w,Tmax}$) is introduced to calculate the more corrected heat of reaction as follows:

$$\Delta H_{o,m,s}=100\varphi(T_{w,Tmax}-T_{o,s})C_sM_s/x \quad (5)$$

where $T_{w,Tmax}$ (K) is the wall temperature of the sample vessel at T_{max} measured by the APTAC. $\Delta H_{o,m,s}$ (Jmol^{-1}) is the corrected heat of reaction obtained using $T_{w,Tmax}$ and $T_{o,s}$.

The relationship between the DTBP concentration and $\Delta H_{o,m,s}$ is shown in Fig. 8. The values of the heat of reaction are converted to that of DTBP 100%. There are the $\Delta H_{o,s}$ values in addition to some measurement examples of the ARC, the APTAC and the DSC in Fig. 8. The heats of reaction of DTBP 38% and DTBP 100% measured by the DSC in this work is 216.8 and 170.9 kJ mol^{-1}, respectively. The $\Delta H_{o,m,s}$ value becomes closer to the values by the ARC and the DSC than ΔH and $\Delta H_{o,s}$. The good agreement between the $\Delta H_{o,m,s}$ value and the heat of reaction by the ARC and DSC value is obtained by the correction of the heat onset and the maximum temperatures.

The correction of the heat onset temperature and the maximum temperature of the APTAC has the effect on the heat of reaction of the DTBP samples with the high concentration. This reason is that the difference between the sample temperature and the vessel wall temperature become large with the increase of the DTBP concentration.

The relationship between the DTBP mass in toluene and the corrected heat of reaction is summarized in Fig. 9. The values of the heat of reaction are converted to that of DTBP 100%. The ΔH values of the small DTBP mass less than 2.4 g become lower by the correction of the heat onset temperature. The $\Delta H_{o,s}$ values of the large DTBP mass more than 4.0 g become lower by the correction of the maximum temperature. The $\Delta H_{o,m,s}$ values are nearly constant and rarely depend on the DTBP mass.

Conclusions

The relationships between the sample mass and the heat onset temperature in the addition to the maximum temperature were investigated to explain the heat of reaction measured by the APTAC. DTBP(di-tert-butyl peroxide)/toluene was chosen as sample. The apparatus properties and the reliability of the data obtained by the APTAC were examined on the basis of the experimental data. The following conclusions were obtained:

- The heat onset temperatures obtained by the APTAC with various sample masses are nearly constant. The heat onset temperature decreases with the increase of DTBP concentration. The maximum temperature increases with the increase of the DTBP mass and the DTBP concentration.
- The heat of reaction values obtained by the APTAC are different from the heat of reaction values by the ARC and the DSC when the method to obtain the heat of reaction by the ARC is applied. When the correction to the heat onset temperature and the maximum temperature obtained by the APTAC is

conducted, the corrected heat of reaction values become close to those obtained by the ARC and the DSC.

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