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Thermal Decomposition Behavior of di-tert-butyl Peroxide Measured with Differential Adiabatic Calorimeter

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A differential adiabatic calorimeter (DAC) was recently 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. Its calorimeter can measure thermal properties of sample regardless of heat capacity of the sample container. There is a possibility that it becomes to the useful tool to estimate the hazards of the self-reactive substances.

The adiabatic temperature rise measured by its calorimeter does not depend on the sample mass experimentally though the adiabatic investigation strongly commonly depends on sample mass. 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 were examined with di-tert-butyl peroxide (DTBP)/toluene solution. DTBP is one of the self-reactive substances and used as standard sample of the ARC (accelerating rate calorimeter). In addition, the property of DTBP decomposition was investigated by the measurements data of the differential adiabatic calorimeter.

As a result of measurements, the measurement results implied DTBP reacted with toluene as the problem of DTBP. In order to solve these problems, it was proposed to use pentadecane as solvent because pentadecane was not so volatile and active in the range of the measurement temperature. The experimental results suggested the DTBP decomposition process depended on DTBP concentration.

The activation energy and heat of reaction obtained by the DAC was almost the same as literature values. In addition, the data of heat rate and the pressure rate without the sample mass and solvent effects were obtained in the thermal decomposition of DTBP.

1. Introduction

Many incidents caused by organic peroxides has been reported in the industrial process (Wu et al. 2008). The organic peroxides led to the runaway reaction, the fire and the explosion in the incident. It is important to evaluate the thermal hazards of the organic peroxides to prevent the incidents. A differential adiabatic calorimeter (DAC) was recently developed to examine the thermal properties for runaway reactions under 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 such as the ARC (accelerating rate calorimeter) (Townsend and Tou, 1980). The phi-factor represents the effect of heat capacity of 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 adiabatic calorimeter with a large sample mass and low heat capacity of the sample container give useful data near the real condition on the storage, its handing and transportation of the sample (Tou and Whiting, 1981).

The DAC has the sample container and the reference container. 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. However, the DAC is not so familiar in the field of the adiabatic investigation and the thermal hazards evaluation. In this report, the measurement results by the

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DAC are studied with di-tert butylperoxide (DTBP). DTBP is one of the self-reactive substances and used as standard sample in the adiabatic investigation such as the ARC. 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 DAC was applied for the evaluation of the solvent effect on the thermal decomposition hazards of using DTBP. The silicone oil and pentadecane were used as solvent in addition to toluene. There were some studies that the solvent effect on the thermal decomposition of DTBP solution was investigated with the Tsu (thermal screening unit) (Maschio et al., 2010) and the RSST (reaction system screening tool) (Saraf et al., 2003) using the other solvents which were different from silicone oil and pentadecane. In addition, the thermal decomposition of DTBP/toluene solution was studied by the data measured with the DAC.

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 both of container masses are 56.8 g. 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 when the sample generates heat more than the threshold for the detection of the DAC. 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 solutions with various mass and concentration were used in the experiments. The purity of DTBP was more than 98 wt.%. Toluene and pentadecane was special grade. Silicone oil was dimethyl silicon oil (KF-963) supplied by Shin-Etsu Chemical Co., Ltd. Its temperature range for usage was from -30 ^{o}C-250 ^{o}C. Toluene, silicone oil and pentadecane were used as solvent. The mass of DTBP solutions used in the tests were 1.0 g, 3.0 g, 5.0 g and 8.0 g. The concentration range of DTBP was between 10wt% and 30wt% in toluene solutions. There were many data on the DTBP15wt%/toluene solution as the standard sample in the adiabatic investigation because DTBP15 wt% solutions with various solvents were measured when the sample mass varied. The all tests were conducted with the sample mass of five grams in the experiments regarding to the decomposition of DTBP in various concentrations.

2.3. Measurement conditions

The threshold to detect an exothermic reaction is 0.01 K/min of the heat rate. The maximum value of heat rate supplied by the DAC is 100 K/min approximately. The sample temperature is automatically incremented by 5 K in the case that the exotherm of more than 0.01 K/min is not detected by the thermocouple of sample container wall. 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.

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

The adiabatic temperature rise (ΔT_{ad} in K) equals (T_{max} - T_o). T_o (K) and T_{max} (K) mean the heat onset temperature and the maximum temperature, respectively. The C_s value is the averaged specific heat of T_o and T_{max} of the sample solution. For example, C_s of DTBP/toluene solution value is obtained from the averaged specific heat for toluene and DTBP as the following Eq.(2).

$$C_s = x \cdot C_{s(DTBP,avg)} + (1-x) \cdot C_{s(tol,avg)} \tag{2}$$

The x(-) value is the ratio of DTBP in DTBP/toluene solution. The x value multiplied by 100 is DTBP concentration(wt%). The $C_{s(DTBP,avg)}$ and $C_{s(tol,avg)}$ values are the specific heat of DTBP and toluene averaged by each temperature closed to T_o and T_{max}, respectively. The range of C_s is from 2.02 to 2.42 J/g/K regarding to DTBP/toluene solution. The specific heat value of silicon oil is the averaged value of the specific heat value of silicon oil measured by the DSC at 100 ^{o}C and 200 ^{o}C. The range of C_s is from 1.83 to 2.14 J/g/K regarding to DTBP/silicon oil solution. The specific heat value of pentadecane is obtained in the same manner. The C_s value of DTBP/pentadecane solution is 2.91 J/g/K.

Though the phi-factor (φ) is one in the DAC, it is defined commonly in the adiabatic investigation as:

$$\varphi = 1 + (M_c \cdot C_c)/(M_s \cdot C_s) \quad (3)$$

The φ value is the phi-factor. M_c (g) is the sample container mass, M_s (g) sample mass, C_c (J/g/K) the sample container specific heat. The C_c value is the specific heats averaged by each temperature closed to T_o and T_{max}. The ΔH (J/g-intake) value is calculated by the following equation in the common adiabatic investigation. ΔH is equals to $C_s \cdot \Delta T_{ad}$ in the DAC because φ is one. The ΔH (J/g-intake) value divided by x is ΔH (J/g-DTBP100%), which is the converted value to the heat of reaction of pure DTBP.

$$\Delta H(J/g\text{-}intake) = \varphi \cdot C_s \cdot \Delta T_{ad} \quad (4)$$

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 (Leung and Fauske, 1986):

$$k = (dT/dt) / (T_{max} - T) \qquad (reaction\ order = 1) \quad (5)$$

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

$$\log k = \log(A) - (1/2.303) \cdot (E/R/T) \quad (6)$$

E is the activation energy (J/mol), k rate constant (1/s), and A is the frequency factor (1/s). R is the gas constant (8.314J/mol/K). E and A are obtained by logk versus 1/T plot. E is the slope and A is the intercept on the straight line.

3. Results and discussion

3.1. Measurement results of DTBP15 wt% toluene solution

Figure 2 shows the typical measurement results of temperature and pressure with the DAC when the heat release is detected. The sample was DTBP 15 wt% pentadecane solution. The sample mass was 5 g. T_o and T_{max} were 131 °C and 182 °C. The maximum heat rate and pressure rate 1.2 K/min and 199 kPa/min DTBP 15 wt% solution with various solvent was used to examine the properties of the DAC. Figure 3 shows the relationship between maximum pressure and sample mass in three solvents. The maximum pressure increased in proportion to the sample mass in all solvents. The vapor pressure of toluene and pentadecane at T_{max} are 749 kPa and 8.1 kPa. The vapor pressure of silicone oil is similar to that of pentadecane. The correction of the vapor pressure was not conducted because their vapor pressures were very small than the pressure by the decomposition gas of DTBP. For example, the vapor pressure of toluene at 250 °C is 1.67 MPa and the highest in the three solvents. Pentadecane is good solvent to evaluate DTBP decomposition without the vapor pressure effect of solvent because its vapor pressure is small.

Figure 4 shows relationship between heat of reaction (J/g-intake) and sample mass in three solvents. The heat of reaction was value per one gram of sample taken for the measurement. The heat of reaction

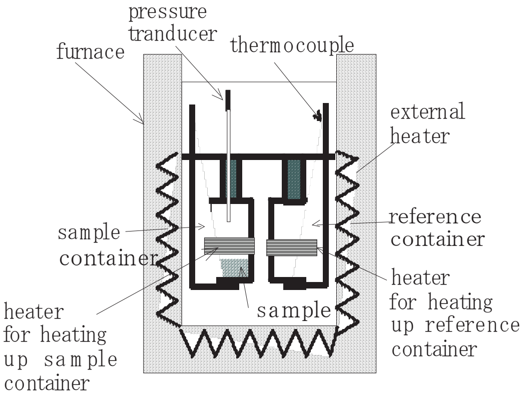

Figure 1 Schematic of differential adiabatic calorimeter

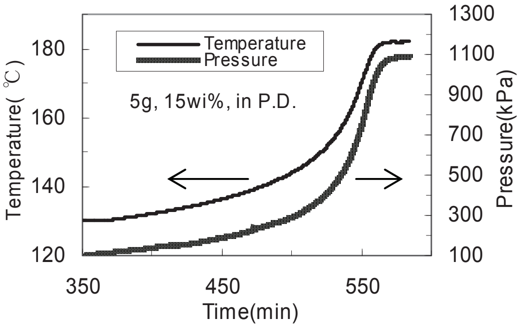

Figure 2 Time history of temperature and pressure measured by the DAC. The sample was DTBP15wt%/pentadecane solution of 5g.

became constant values more than five grams of sample mass in all solvents. There was not large difference in heat of reaction in three solvents. The heat of reaction of DTBP15 wt%/toluene solution was 150 J/g-intake in the constant range. It was suggested the sample mass of more than five grams was required to obtain the appropriate heat of reaction. The relationship between the heat rate and the sample mass was investigated. The maximum heat rate did not very largely increase beyond five grams in all solutions. The result showed the maximum heat rate did not depend on the sample mass in more than five grams.

Figure 5 shows relationship between logk and 1/T. The straight line was obtained assumed the first-order reaction. The temperature range used for the calculation of E in Figure 5 was 132 °C to 171 °C. It suggested the reaction of DTBP decomposition progressed in the first-order reaction.

3.2. Decomposition of DTBP in various concentrations

Figure 6 shows relationship between E and DTBP concentration. The E was almost same value within the range from 10 wt% to 30 wt% in three solvents. The E value obtained in pentadecane, silicone oil and toluene were 170.3 kJ/mol, 158.5 kJ/mol and 155.3 kJ/mol. The reference value measure by the ARC using DTBP15 wt%/toluene solution was 157.3 kJ/mol (Kersten et al, 2005). The E value obtained with Phi-Tec of the other adiabatic calorimeter was 158.5 kJ/mol (Kersten et al, 2005). The E value obtained in toluene by the DAC was similar to the reference value. It was elucidated the E value obtained by the DAC was appropriate and reliable.

Figure 7 shows relationship between T_o and DTBP concentration. The T_o value decreased in toluene and silicone solution when DTBP concentration increased. T_o was constant in pentadecane solution when DTBP concentration increased. This results showed toluene and silicone oil already began to react with DTBP at T_o though pentadecane did not react with DTBP. Pentadecane was good solvent in order to examine DTBP decomposition because it was stable chemically and difficult to react with chemical

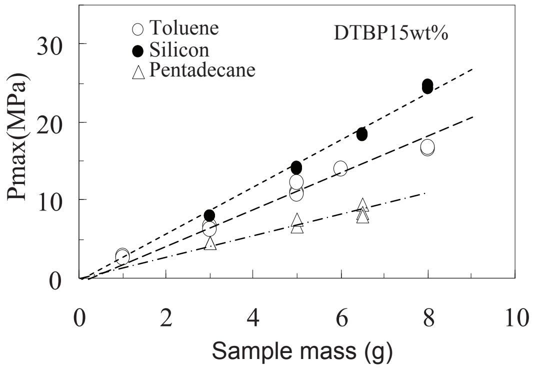

Figure 3 Relationship between maximum pressure and sample mass.

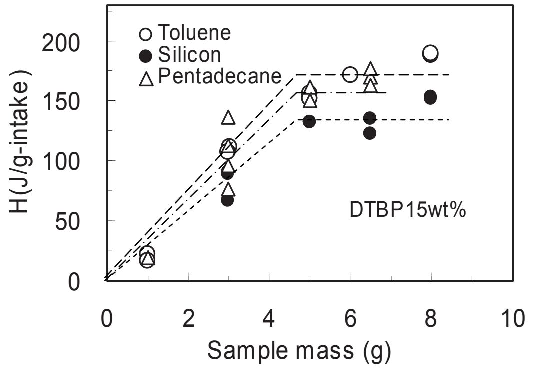

Figure 4 Relationship between heat of reaction and sample mass.

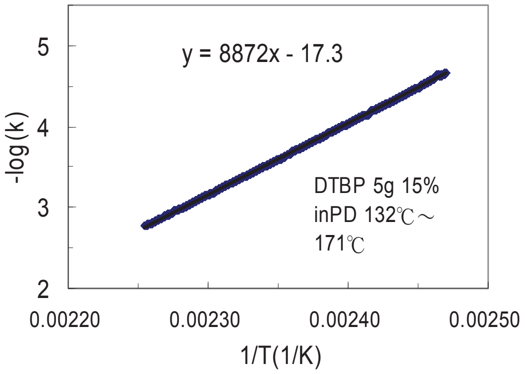

Figure 5 Relationship between logk and 1/T. The sample was DTBP15wt%/pentadecane solution of 5g.

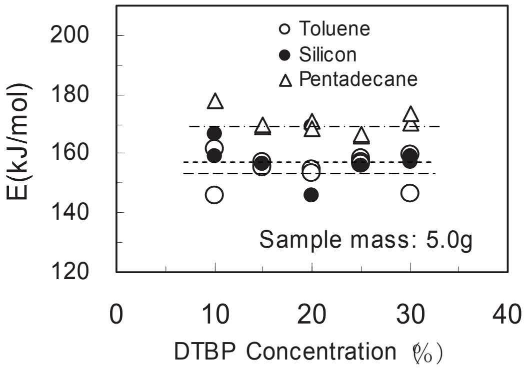

Figure 6 Relationship between activation energy and DTBP concentration.

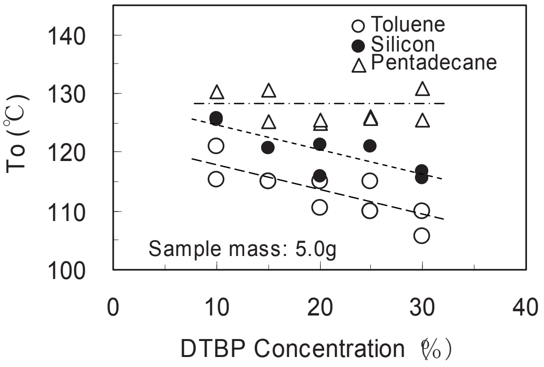

Figure 7 Relationship between heat onset temperature and DTBP concentration.

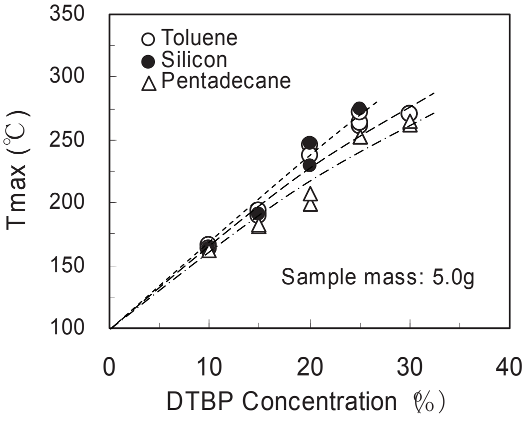

Figure 8 Relationship between maximum temperature and. DTBP concentration.

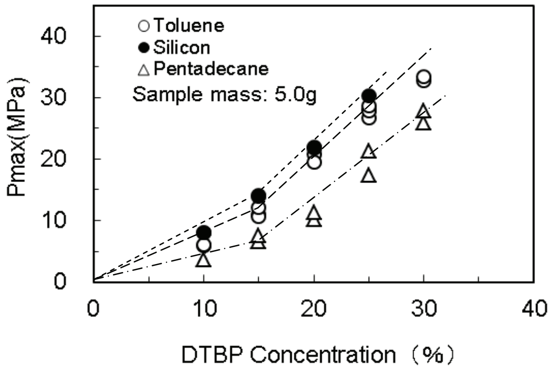

Figure 9 Relationship between the maximum pressure and DTBP concentration.

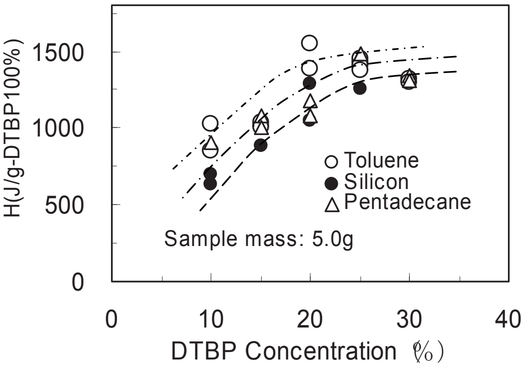

Figure 10 Relationship between heat of reaction and DTBP concentration.

substances in addition to its small vapor pressure.

Figure 8 shows the relationship between the maximum temperature and DTBP concentration. The data of DTBP 30 wt% of 5 g in silicon oil were deleted because it was found silicon oil reacted with DTBP 30 wt% toluene solution on the basis of the measurement data of TG-DTA. The straight line was obtained from the proportional relationship between T_{max} and DTBP concentration from the zero to 20 wt% in all solutions. The slope of the straight line decreased beyond 20 wt% in toluene and pentadecane solutions.

Figure 9 shows the relationship between the maximum pressure and DTBP concentration. The slope from 15 wt% to 30 wt% was larger than the slope from the zero to 15 wt% in three solutions. This tendency was conspicuous when pentadecane did not react with DTBP in DTBP/pentadecane solution. This result suggested there the process of DTBP decomposition varied near 15wt% of DTBP concentration.

Figure 10 shows the relationship between the converted heat of reaction to pure DTBP and DTBP concentration. The sample mass was 5.0 g. This sample mass was enough to measure the heat of reaction from result of Figure 4. The converted heat of reaction became almost constant beyond 20 wt%.The obtained value was 1.32 kJ/g-DTBP100 % using DTBP 30 wt% in toluene. This value was almost the same as to the heat of reaction of pure DTBP measured by the DSC (1.18 kJ/g). It was also almost the same as the heat of reaction (1.17 kJ/g-DTBP 100 %) of DTBP 30 wt% toluene solution obtained with the ARC (Aldeeb et al., 2002).

The converted heat of reaction should be constant regardless of the DTBP concentration if DTBP decompose process did not depend on the DTBP concentration. The result of Figure 10 showed the decomposition process from the zero to 20 wt% was different from the decomposition process from 20wt% to 30 wt%. This result was consistent with the suggestion deduced from the result of Figure 9. It was predicted the activation energy of decomposition in the low DTBP concentration (0 – about 20 wt%) was similar to the value in the high DTBP concentration (about 20 – 30 wt%).

Figures 11 and 12 show the relationship between the maximum heat rate in addition to pressure rate and DTBP concentration. HR_{max} of 30wt% did not increase compared with the values of 20 wt% and 25 wt% in all solutions. This reason was that the DAC could not supply the heat more than about 100 K/min of heat rate to maintain the adiabatic condition. On the other hand, the pressure rate increased exponentially at 30 wt%. compared with the values of 20 wt% and 25 wt% in all solutions. The pressure rate data was valid for evaluation hazards within the range of the intense reaction.

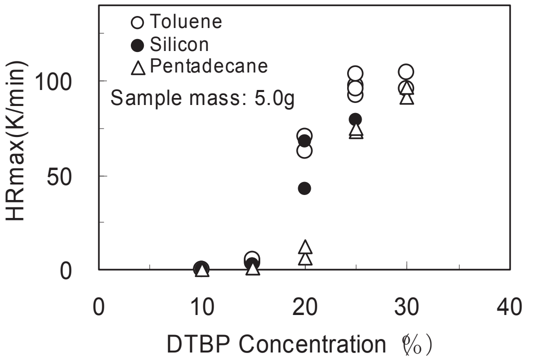

Figure 11: Relationship between maximum heat rate and DTBP concentration

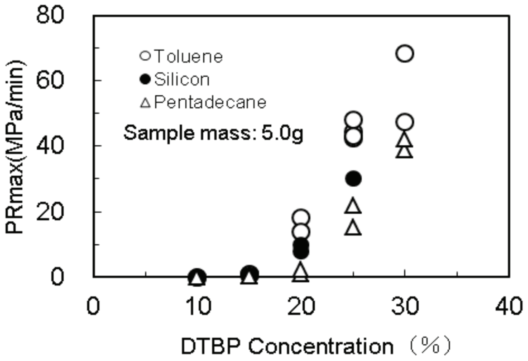

Figure 12: Relationship between maximum pressure rate and DTBP concentration.

4. Conclusions

The measure method by the differential adiabatic calorimeter (DAC) was investigated using DTBP solution of toluene, silicone oil and pentadecane. The followings conclusions were made:

(1) The sample mass was needed in more than five grams to obtain the appropriate heat of reaction. The activation energy and the heat of reaction measured by the DAC were appropriate compared with the values by the DSC and the ARC within the range from 10 wt% to 30 wt% of DTBP solutions.

(2) DTBP reacted with toluene and silicone oil from the heat onset temperature. Pentadecane was good solution for estimating and studying the decomposition of DTBP because it did not react with DTBP and its vapor pressure was small. The DTBP decomposition process depended on the DTBP concentration in three solutions.

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