Article

Risk evaluation by pressure rise measured using adiabatic calorimeter

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Abstract

An automatic pressure tracking adiabatic calorimeter (APTAC) had been developed to obtain the thermokinetic and the vapor pressure data during runaway reactions. It is important to conduct a risk evaluation using the heat rate and the pressure rate in decomposition in order to handle chemical material safely. The APTAC is an adiabatic calorimeter with a large-scale sample weight and low thermal inertia. Pressure is generated outside the sample cell to cancel the pressure difference during a reaction. The APTAC is a useful tool for assessing thermal hazards of reactive chemicals. The data obtained by the APTAC is important information for the design for the safe industrial process. The pressure data is one of the necessary parameters to design a reactor and a safety vent. However, the data by the APTAC is not familiar because there are few measurement examples and papers regarding the APTAC.

The data of di-tert-butyl peroxide (DTBP) / toluene solutions are collected by the APTAC. The relationship between the sample weight and the pressure rise is examined. The influence of the DTBP concentration on the pressure and the pressure rate is investigated. The reasonable method to evaluate the intensity of the decomposition is derived on the base of the pressure rate data.

Keywords: Thermal decomposition, Automatic pressure tracking adiabatic calorimeter, Pressure, Pressure rate

1. Introduction

An adiabatic calorimeter can provide data for evaluating potential hazards of reactive chemicals. The measurement results are useful for safety storage, handling and transportation of chemicals. An automatic pressure tracking adiabatic calorimeter (APTAC) is an adiabatic calorimeter with a large- scale sample weight and low thermal inertia[1]. The principle of the adiabatic system is the same as an accelerating rate calorimeter (ARC). The pressure outside the sample cell is controlled to cancel the generated pressure inside the sample cell to cancel the pressure difference during a reaction.

The pressure and the heat rate data can be obtained by the APTAC. The pressure data is important information for the evaluation of thermal hazards of reactive chemicals and the design for the safe industrial process. The risk evaluation of chemicals on the basis of the pressure data are discussed by some papers[2, 3]. The analysis of the runaway reaction was conducted by the pressure data measured by the ARC[4]. The pressure data for the pressure relief design are essential for accomplishing safety for a reactor.

Some examples of the risk evaluation of a chemical substance by the APTAC were known[5, 6]. However, the pressure data obtained by the APTAC are not so familiar because there are not so many reports of risk evaluation by the APTAC. Therefore the data of di-tert-butyl peroxide (DTBP) / toluene solutions collected by the APTAC are examined. DTBP / toluene solutions are used as the standard sample to have the knowledge of the properties of data by the ARC[7]. The relationship between the sample weight and the pressure is examined. The reasonable method to evaluate the intensity of the decomposition is discussed on the base of the pressure rate data.

2. Experimental
2.1. 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 cell wall and the ambient temperature. The thermocouple for sample is inserted by a Teflon tube in order
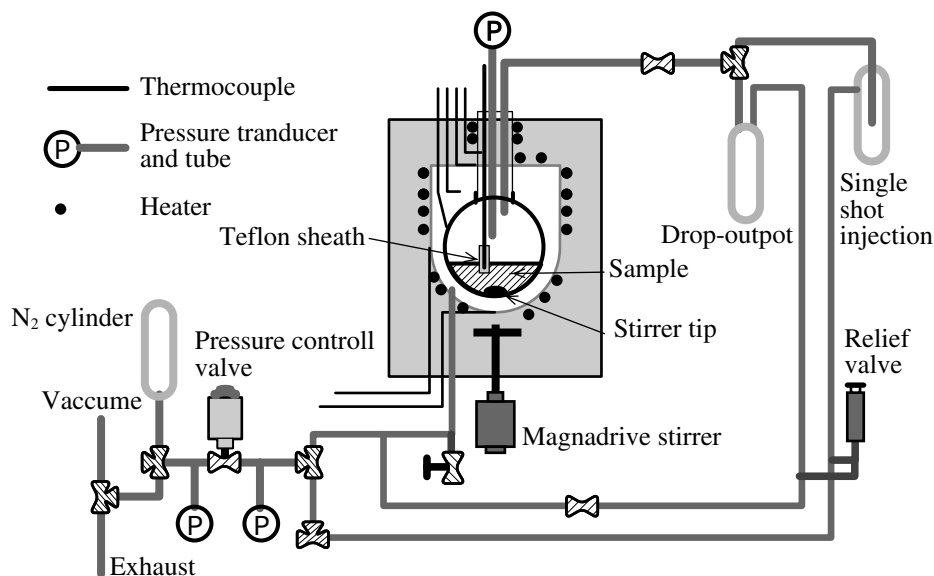
Fig. 1 Outline of APTAC apparatus.

to reduce the catalytic effect by the surface thermocouple. The spherical sample cell is screwed at the top heater and the sample thermocouple passes directly into the sample cell 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 achieved by maintaining the sample and the ambient temperatures exactly equal. Reactions can be followed up to about 400 K min^{-1}. Because the pressure outside the sample cell is controlled to equal to the pressure inside the sample cell, the glass cells and the sample cells with low thermal inertia of a large- scale weight can be used in the experiments.

2.2. Samples

Volume of the sample cell was 130 cm^3. The pressure rise inside the sample vessel by DTBP / toluene solutions was measured by the APTAC. The concentration range of DTBP / toluene solutions was from 20 wt.% to 60 wt.%. Sample weights of DTBP / toluene solution were from 3 g to 40 g. The range of the φ-factor was between 1.8 and 9.1. The φ-factor is the dimensionless thermal inertia factor for the sample cell. The φ-factor is defined as the following equation.

$$\varphi\text{-factor} = (C_{p,sol}\cdot W_{,sol} + C_{p,v}\cdot W_{,v}) / (C_{p,sol}\cdot W_{,sol}). \quad (1)$$

$C_{p,sol}$: heat capacity of DTBP / toluene solution (J/g/K)
$C_{p,v}$:   heat capacity of sample vessel (J/g/K)
$W_{,sol}$: weight of DTBP / toluene solution (g)
$W_{,v}$:   weight of sample vessel (g)

2.3. Measurement conditions

All experiments were performed in a closed cell environment with ambient air above the sample. Borosilicate glass sample cells were used in the measurement. The threshold to detect an exothermic reaction was 0.05 K min^{-1} of the heat rate. The sample temperature was automatically incremented by 10 K. The pressure rise inside the sample cells during the reactions was followed up to about 7,500 kPa of the pressure and 75,000 kPa min^{-1} of the pressure rate. The filling ratio was applied to the correction of the pressure and the pressure rate for considering the sample volume. The filling ratio (r) was obtained by dividing the sample volume by 130. The sample volume was calculated using their densities and the weight ratio in solution. The [Pressure]·r value and the [Pressure rate]·r value are needed to estimate the pressure and the pressure rate in the sample cell volume (130 cm^3), respectively. A subscript of r expresses the correction of the filling ratio.
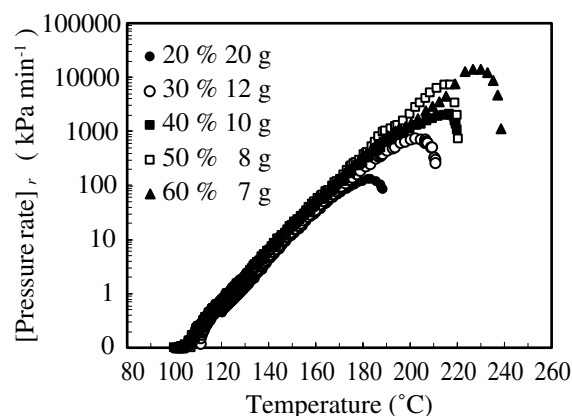

Fig. 2 Corrected pressure rate vs. sample temperature for DTBP decomposition measured by APTAC.
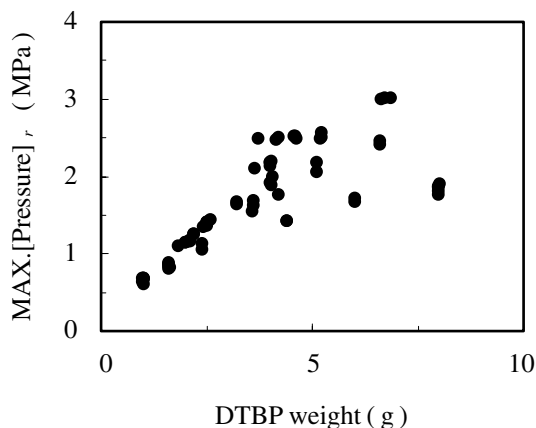
Fig. 3 Relationship between DTBP weight in toluene and maximum of corrected pressure. DTBP concentrations are from 20 wt.% to 60 wt.%.
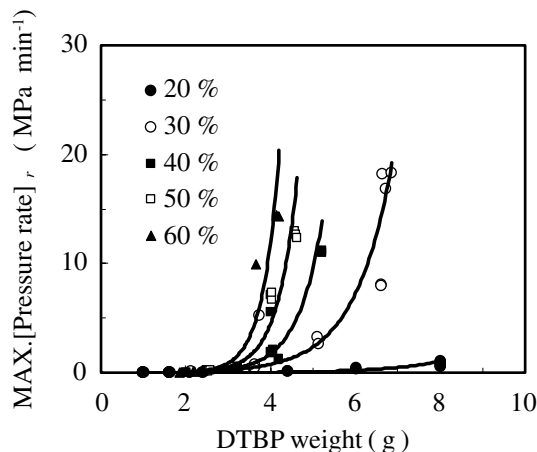

Fig. 4 Relationship between DTBP weight in toluene and maximum of corrected pressure rate.

3. Results and Discussion
3.1. Maximum of pressure

The pressure rise occurred by the decomposition of DTBP with various concentrations in toluene was measured by the APTAC. Figure 1 shows examples of the corrected measurement results of pressure. The horizontal axis is the sample temperature. The vertical axis is the logarithm of the corrected pressure rate. The corrected pressure rate of DTBP 60 wt.% increased with the larger rate to the sample temperature, compared with those of the other samples when the sample temperature was beyond 200 °C.

Pressure is one of the parameters for estimating the intense of decomposition when the self-reactive substance reacts. Figure 2 shows the relationship between the maximum of the corrected pressure and the DTBP weight in toluene. The maximum of the corrected pressure was recorded closely to the maximum of temperature in the decomposition of DTBP. DTBP concentrations are from 20 wt.% to 60 wt.%. The DTBP weight is calculated by [the sample weight] · [DTBP concentration] / 100 [g]. The maximum of the corrected pressure increases with the weight of DTBP in toluene proportionally. It is elucidated that the maximum of the corrected pressure relates with the amount of the generated gas. The maximum of the corrected pressure can be predicted by the weight of the self-reactive substance in solution.

3.2. Maximum of pressure rate

The pressure rate is one of the important parameters which indicate the intense of decomposition when the self-reactive substance reacts. Figure 3 shows the relationship between the maximum of the corrected pressure rate and the DTBP weight in toluene. The curve fitting by the exponential approximation was applied to the corrected pressure rate data. The maximum of the corrected pressure rate increases with the weight of DTBP in toluene exponentially. It is elucidated that the maximum of the correct-

ed pressure rate is influenced by the weight of DTBP. The corrected pressure rate can be expressed as follows as *a* result of the curve fitting.

$$[\text{Pressure rate}]_r = b \cdot \text{EXP}\,(a \cdot [\text{DTBP weight}])\,. \qquad (2)$$

The units of the corrected pressure rate and DTBP weight are kPa min^{-1} and gram, respectively. *a* and *b* are constants. The constants *a* and *b* are obtained by the exponential approximation. The constant *b* is corresponded to zero of DTBP weight. The constant *b* is assumed that it expresses the vapor pressure rise toluene of solvent.

The constant *a* is investigated in relation to the DTBP concentration. The relationship between constant and the DTBP concentration is shown in Fig. 4. The constant *a* increases proportionally with the increase of the DTBP concentration. The constant *a* is obtained if the DTBP concentration is known. The maximum of the corrected pressure rate is calculated on the basis of the DTBP weight in toluene. The maximum of the corrected pressure rate can be predicted by concentration and the weight of the self-reactive substance in solution.

The maximum of the corrected pressure and corrected pressure rate are the measurement values in the solution system of DTBP / toluene. The measurement results involve the vapor pressure of DTBP and toluene in addition to the pressure rise by the decomposition of DTBP in a gas phase. The maximum of the pressure and the pressure rate measured are useful for the risk evaluation regarding the whole of the DTBP / toluene solution.

The relationships between the corrected pressure and the corrected pressure rate in DTBP 40 wt.% and DTBP 50 wt.% are shown in Figs. 5, 6. The corrected pressure rate curves are drawn in figures prior to the corrected pressure decrease points. The vertical axis is the logarithms of the corrected pressure rate. The corrected pressure rates of DTBP / toluene solution with various sample weight and concentrations were measured. The corrected pressure rate
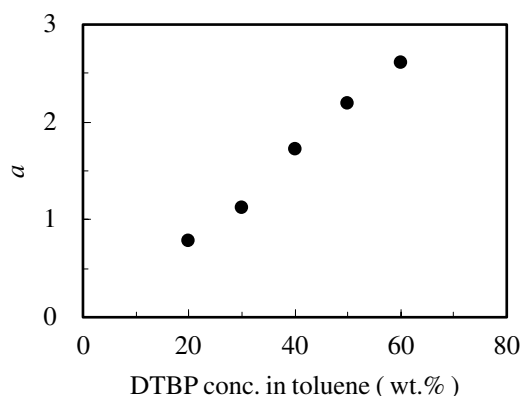
Fig. 5 Relationship between DTBP concentration and constant a calculated by exponential approximation of the maximum of corrected pressure rate.
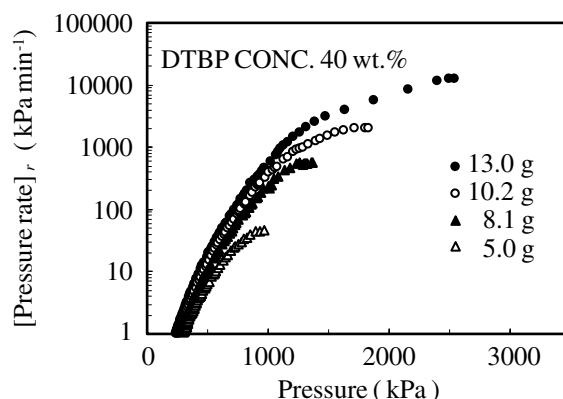

Fig. 6 Relationship between corrected pressure and corrected pressure rate in DTBP 40 wt.% solution with various sample weight.
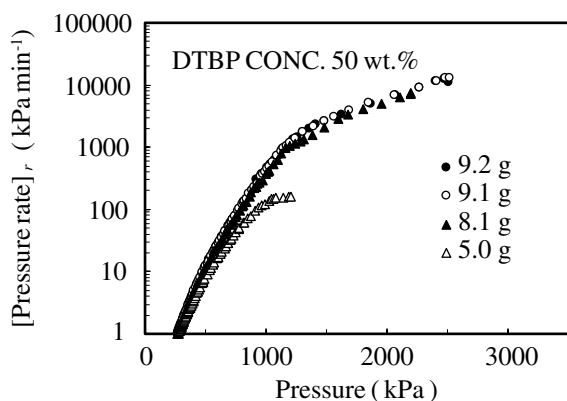

Fig. 7 Relationship between corrected pressure and corrected pressure rate in DTBP 50 wt.% solution with various sample weight.

can be expressed using the following equation[8].

$$[\text{Pressure rate}]_r = \text{EXP}(\alpha \cdot ([\text{Pressure}]_r - [\text{Initial pressure}]_r)). \quad (3)$$

α is a constant. The units of the corrected pressure rate and the corrected pressure are kPa min^{-1} and kPa, respectively. The results show the sample weight influences on the curves of the corrected pressure rate on the same concentration condition. The corrected pressure rate curves extend when the samples with the large weight are measured. The reproductivity of data with the weight of 9.1 g and 9.2 g is good from the results of Fig. 7. The first stage of the corrected pressure rate appears to be distinguished from the second stage on the basis of the slope of the corrected pressure rate against the corrected pressure when the sample weight increases. The slopes of the corrected pressure rate to the corrected pressure with two stages are summarized in Table 1. The corrected pressure points at which the first stage transfers to the second stage are 0.5 - 0.6 times than the maximum of the corrected pressure. The slope of the first stage is 1.8 - 5.0 times larger than the slope of the second stage. Table 1 shows the sample weights at which the sample begins to have the second stage in the various DTBP concentrations. Those sample

Table 1 Slope of corrected pressure rate to corrected pressure with two stages in sample of various DTBP concentrations.

DTBP concentration (%)	Sample weight (g)	End [Pressure]$_r$ of first stage (kPa)	Max. [Pressure]$_r$ (kPa)	Slope	
				First stage slope	Second stage slope
20	40.0	780	1400	0.0023	0.0013
30	22.1	1300	2900	0.0032	0.00064
40	10.0	1100	1800	0.0034	0.00089
50	9.2	1200	2500	0.0033	0.00077
60	7.0	1200	2500	0.0033	0.00085

weights decrease when the DTBP concentration increases from 20 wt.% to 60 wt.% in toluene.

4. Conclusions

The decomposition of DTBP / toluene solutions was investigated on the basis of the pressure data obtained by the APTAC. The following conclusions are made:

(1) The maximum of the corrected pressure increases with the weigh of DTBP in toluene proportionally. It is elucidated that the maximum of the corrected pressure relates with the amount of the generated gas. The maximum of the corrected pressure can be predicted by the weight of the self-reactive substance in solution.

(2) The corrected pressure rate data can be fitted by DTBP weight using the exponential approximation. The maximum of the corrected pressure rate increases with the weight of DTBP in toluene exponentially. It is elucidated that the maximum of the corrected pressure rate is influenced by the weight of DTBP. The maximum of the corrected pressure rate can be predicted by the concentration and the weight of the self-reactive substance in solution.

(3) The corrected pressure rate curves extend against the corrected pressure when the sample weight increases. The first stage of the corrected pressure rate appears to be distinguished from the second stage on the basis of the slope of the corrected pressure rate against the corrected pressure when the sample weight increases.

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断熱型熱量計を用いた圧力上昇による危険性評価

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断熱型圧力追従式熱量計（APTAC）は暴走反応中の熱力学および圧力データを得るために開発された。化学物質を安全に取り扱うために，分解時の発熱速度および圧力上昇速度を用いて危険性評価を行うことは重要である。APTACは比較的多くの試料量，すなわち小さな熱補正係数の条件で測定ができる断熱型熱量計である。反応中に生じる試料容器内外の圧力差が無くなるように試料容器外の圧力が調整される。APTACは反応性物質の熱的危険性を評価するために有用な装置である。APTACによって得られるデータは安全な産業プロセスの構築のための重要な情報である。圧力データは反応器および安全弁の設計に不可欠な要素の一つである。しかし，APTACに関する測定例および論文は少ないため，APTACによるデータはあまり知られていない。

APTACを用いて過酸化ジ-tert-ブチル（DTBP）／トルエン溶液の測定が行われる。試料重量と圧力上昇の関係が調べられる。DTBP濃度の圧力および圧力上昇速度の影響が検討される。圧力上昇速度のデータを基にして分解の激しさを評価する合理的な方法が導き出される。

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