

Risk evaluation on the basis of pressure rate measured by automatic pressure tracking adiabatic calorimeter

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Abstract

An automatic pressure tracking adiabatic calorimeter (APTAC) had been employed to obtain the thermokinetic and the vapor pressure data during runaway reactions. The APTAC is an adiabatic calorimeter with a large-scale sample mass and low thermal inertia, and is an extremely useful tool for assessing thermal hazards of reactive chemicals. The data obtained by the APTAC are important information for the design of the safe industrial process.

The thermodynamics parameters and the gas production were discussed on the basis of the experimental data of various concentrations and weights of di-*tert*-butyl peroxide (DTBP)/toluene solution for the purpose of investigating the properties of the APTAC data. The thermal decomposition of DTBP was studied on the basis of the temperature data and the pressure data obtained by the APTAC. The activation energy and the frequency factor of DTBP are nearly constant and the same as the literature values in the concentrations between 20 and 60 wt.%. The pressure rise due to gas production is important data for designing the relief vent of a reactor. The time history of the gas production was investigated with various weights and concentrations. The total gas production index, which had the vapor pressure correction, was 1.0 in the decomposition of DTBP.

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1. Introduction

An adiabatic calorimeter can provide data for evaluating potential hazards of reactive chemicals. The measurement results are useful for the safe storage, handling and transportation of chemicals. The automatic pressure tracking adiabatic calorimeter (APTAC) is an adiabatic calorimeter with a large-scale sample mass and low thermal inertia [1]. The APTAC had been used in order to estimate the hazards of the thermal decomposition of the reactive substances [2]. The adiabatic control system is the same as the 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 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.

However, the measurement data with the APTAC are limited and not enough for discussing the properties of the APTAC data in detail. The thermal decomposition of di-*tert*-butyl peroxide (DTBP) was investigated in order to examine the temperature data and the pressure data of the APTAC [3,4]. The thermodynamics parameters and the gas production were discussed on the basis of the experimental data of various concentrations and weights of DTBP/toluene solution. The analysis and the evaluation method of the pressure data were emphasized in this paper. The pressure data is important for designing the pressure relief in the chemical reactor. In addition, the thermal decomposition of DTBP was studied on the basis of the experimental data.

2. Experimental

2.1. Apparatus

Fig. 1 shows an outline of the APTAC calorimeter schematically. Three N-type thermocouples are used to measure the temperature inside the sample, the surface temperature of the sample cell wall and the ambient temperature. The measured

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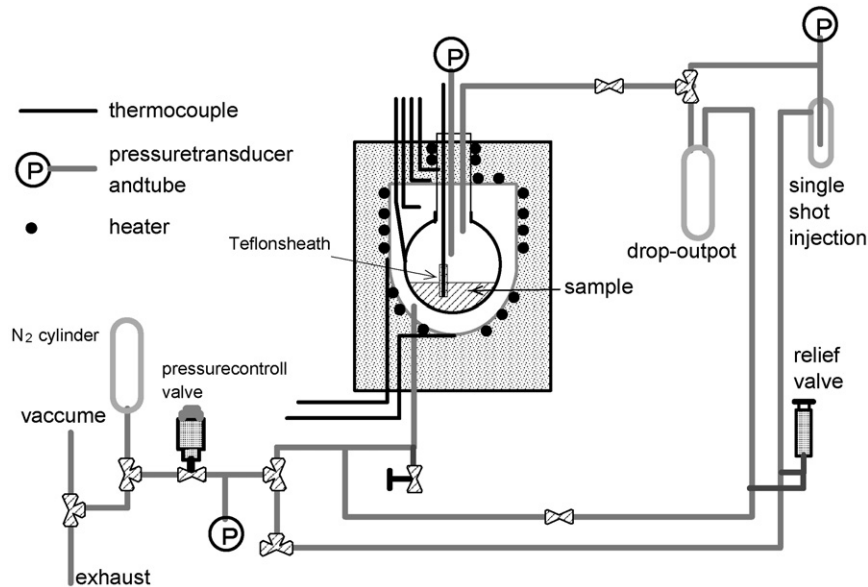


Fig. 1. Outline of APTAC apparatus.

sample temperature is used in the adiabatic control. 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 making the sample and the ambient temperatures exactly equal. The APTAC detects the temperature inside the sample and controls the adiabatic conditions by the sample temperature.

Because the pressure outside the sample cell is controlled to be equal to the pressure occurred inside the sample cell by the reaction, the glass cells such as made of weak materials or the sample cells 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 upper limit of the sample mass depends on the heat rate and the pressure rate. The φ -factor is defined as

$$\varphi = 1 + \frac{M_c C_c}{M_s C_s} \quad (1)$$

M_c (g) is the sample cell mass, M_s (g) the sample mass, C_c (J/(g K)) the sample cell specific heat, and C_s (J/(g K)) is the sample specific heat. The C_c and C_s values are the specific heats averaged by each temperature closed to the heat onset temperature and the maximum temperature. The data of the specific heat are obtained in the literature [5].

2.2. Samples

All experiments were performed in a closed cell 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 operation of the ARC data [6]. The range of DTBP concentrations is between 20

and 60 wt.% in the DTBP/toluene solution. Sample weights of DTBP/toluene solution are from 3.1 to 40.0 g. The range of the φ -factors is between 1.8 and 9.1.

2.3. Measurement conditions

Volume of the glass sample cell is 130 cm³. The borosilicate glass sample cells 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 of the heat rate. The sample temperature is automatically incremented by 10 K in the case that the exotherm more than 0.05 K/min is not detected by the thermocouple inside sample. The shut down criteria of heat rate is 400 K/min. It depends on the heating ability by the heaters of the APTAC. Pressure rise inside the sample cells during the reactions are followed up to about 7500 kPa of the pressure and 75,000 kPa/min of the pressure rate.

2.4. Decomposition kinetics

When the reaction order is 1, k is expressed by the following the equation [3]:

$$k = \frac{dT/dt}{T_{\max} - T} \quad (\text{reaction order} = 1). \quad (2)$$

T is the sample temperature (K) and T_{\max} is the maximum temperature (K). These temperatures are measured experimentally. The activation energy and the frequency factor are expressed by the following equation:

$$\log(k) = \log(A) - (E/2.303RT). \quad (3)$$

E is the activation energy (J/mol), k is the rate constant (1/s), and A is the frequency factor (s^{-1}). R is the gas constant (8.314 J/(mol K)). E and A obtained by $\log(k)$ versus $(1/T)$ plot [3]. E is the slope and A is the intercept on the straight line.

2.5. Pressure and gas production

The sample volume is calculated using their densities and the weight ratio in solution. The corrected volume is calculated by subtracting the sample volume from the sample vessel volume (130 cm^3) and used in the analysis. All volume data are corrected regarding to the sample volume.

The gas production rate of the noncondensable decomposition gas production is expressed by the following equation:

$$\left(\frac{dn}{dt}\right) = \left(\frac{V}{RT}\right) \left[\left(\frac{dP}{dt}\right) - \left(\frac{P}{T}\right) \left(\frac{dT}{dt}\right)\right]. \quad (4)$$

The (dn/dt) value is the gas production rate of the noncondensable decomposition gas production (mol/min). P is the pressure (Pa). The (dP/dt) value is the pressure rate (Pa/min). T is the sample temperature (K). The (dT/dt) value is the heat rate (K/min). These values are the measured data with the APTAC. The (dn/dt) value is the gas production rate from DTBP/toluene solution. The (dn/dt) value involves the vapor pressure of DTBP/toluene solution. The measured pressure (P) involves the pressure of the filling gas and the vapor pressure of DTBP and toluene due to the vapor–liquid equilibrium in addition to the pressure generated by the production gas in Eq. (4).

The vapor pressure for the DTBP and toluene in the vapor–liquid equilibrium is calculated on the Antoine equation [5]. The vapor pressure correction regarding to DTBP and toluene is applied to the measured pressure data. The calculated vapor pressure of DTBP and toluene is subtracted from the measured pressure data to obtain the corrected pressure. P_{ac} indicates the pressure with the correction of vapor pressure from DTBP/toluene solution. P_{ac} is the total pressure of the noncondensable decomposition gas and the filling gas. The (dP_{ac}/dt) value is obtained by dividing the P_{ac} change by the corresponded time interval. The (dn_{ac}/dt) value is the corrected gas production rate. A subscript of ac expresses the correction of the vapor pressure correction. The similar equation as Eq. (4) is expressed using (dn_{ac}/dt) , P_{ac} and (dP_{ac}/dt) by the following equation:

$$\left(\frac{dn_{ac}}{dt}\right) = \left(\frac{V}{RT}\right) \left[\left(\frac{dP_{ac}}{dt}\right) - \left(\frac{P_{ac}}{T}\right) \left(\frac{dT}{dt}\right)\right]. \quad (5)$$

The DTBP decomposition reaction is assumed to be the first-order reaction. The DTBP concentration can be represented by the following equation in the adiabatic condition:

$$x = \frac{x_0(T_{\max} - T)}{T_{\max} - T_{\text{onset}}}, \quad (6)$$

where x is the DTBP mass fraction in reaction, x_0 is the initial DTBP mass fraction, T_{\max} is the maximum temperature, and T_{onset} is the heat onset temperature.

The mass loss rate of DTBP at the certain temperature is given by the following equation:

$$-\left(\frac{dm}{dt}\right) = m_0 \cdot x \cdot k, \quad (7)$$

where (dm/dt) is the mass loss rate of DTBP and the m_0 is the initial DTBP weight (g). The mass loss rate can be calculated with the kinetic parameters and the temperature data obtained by the APTAC.

One can express the gas production index (N_{ncg}) using the production rate of the noncondensable decomposition gas without the vapor pressure correction (dn/dt) and the mass loss rate by the following equation:

$$N_{\text{ncg}} = -\left(\frac{dn}{dt}\right) \frac{Mw}{dm/dt}, \quad (8)$$

where N_{ncg} is the gas production index without the vapor pressure correction and Mw is molecular weight of DTBP (146.22 g). N_{ncg} shows the mole ratio of the gas production occurred by the decomposition of DTBP to DTBP contained in the sample without the vapor pressure correction. N_{ncg} is variable for the elapsed time in the measurement.

The Δn (mol) value is an amount of the noncondensable decomposition gas production occurred during the measured time interval (min) from t_1 to t_2 of the APTAC as the following equation:

$$\Delta n = \left(\frac{dn}{dt}\right) \Delta t. \quad (9)$$

An amount of the noncondensable decomposition gas production at a certain time, t_1 is represented by Δn . The Δn value involves the vapor pressure correction.

The total amount of the noncondensable decomposition gas production without the vapor pressure correction, n_{total} during the reaction is calculated as the following equation:

$$\Delta n_{\text{total}} = \sum_{t_0}^{t_{\max}} \Delta n. \quad (10)$$

The t_0 and t_{\max} values express the times close to the heat onset temperature and T_{\max} . The gas production index at the maximum mass loss rate ($N_{\text{ncg,max}}$) is used for evaluating the intensity of the gas production. The $N_{\text{ncg,max}}$ involves the vapor pressure of DTBP/toluene solution. The time of $(dm/dt)_{\max}$ should correspond to the same time with the time of $(dn/dt)_{\max}$ in the ideal condition in the experiments. The $(dm/dt)_{\max}$ value is the maximum mass loss rate. $N_{\text{ncg,max}}$ is calculated using $(dm/dt)_{\max}$ and $(dn/dt)_{\max}$ though there is the time difference between the $(dm/dt)_{\max}$ and $(dn/dt)_{\max}$ in the actual experimental results. The $N_{\text{ncg,max}}$ is defined as the following equation:

$$N_{\text{ncg,max}} = -\left(\frac{dn}{dt}\right)_{\max} \frac{Mw}{(dm/dt)_{\max}}, \quad (11)$$

where $(dn/dt)_{\max}$ is the maximum gas production rate of the noncondensable decomposition gas and $(dm/dt)_{\max}$ is the maximum mass loss rate.

The total gas production index ($N_{\text{ncg,total}}$) can be expressed by the total of the noncondensable gas production (Δn_{total}) as the following equation:

$$N_{\text{ncg,total}} = \frac{\Delta n_{\text{total}} \cdot \text{Mw}}{m_0} \quad (12)$$

The $N_{\text{ncg,total}}$ is the intrinsic parameter in the gas production generated by the thermal decomposition of DTBP. N_{ncg} , $N_{\text{ncg,max}}$ and the $N_{\text{ncg,total}}$ are dimensionless. $N_{\text{ncg,max}}$ and $N_{\text{ncg,total}}$ are constants for one measurement.

When the correction of the vapor pressure is applied, Eqs. (13)–(17) are expressed by in the similar way to Eqs. (8)–(12). A subscript of ac indicates the vapor pressure correction. The vapor pressure from DTBP/toluene solution is excluded in the $N_{\text{ncg,ac}}$, Δn_{ac} , $\Delta n_{\text{ac,total}}$, $N_{\text{ncg,ac,max}}$ and $N_{\text{ncg,ac,total}}$ values:

$$N_{\text{ncg,ac}} = - \left(\frac{dn_{\text{ac}}}{dt} \right) \frac{\text{Mw}}{dm/dt}, \quad (13)$$

$$\Delta n_{\text{ac}} = \left(\frac{dn_{\text{ac}}}{dt} \right) \Delta t, \quad (14)$$

$$\Delta n_{\text{ac,total}} = \sum_{t_0}^{t_{\text{max}}} \Delta n_{\text{ac}}, \quad (15)$$

$$N_{\text{ncg,ac,max}} = - \left(\frac{dn_{\text{ac}}}{dt} \right)_{\text{max}} \frac{\text{Mw}}{(dm/dt)_{\text{max}}}, \quad (16)$$

$$N_{\text{ncg,ac,total}} = \Delta n_{\text{ac,total}} \frac{\text{Mw}}{m_0}. \quad (17)$$

3. Results and discussion

3.1. Heat rate and pressure rate of DTBP

A number of experiments were conducted using DTBP/toluene solution to investigate the properties of the APTAC and the DTBP decomposition. The APTAC detects the temperature inside the sample and controls the adiabatic conditions by the sample temperature. The sensibility and the response of the APTAC are better than those of the equipments

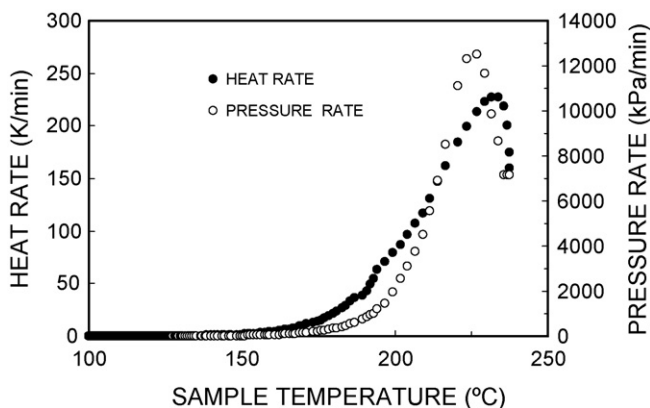


Fig. 2. The heat rate and the pressure rate measured by APTAC. The sample is DTBP 40 wt.%/toluene solution. The sample weight is 13.0 g ($\varphi = 3.1$).

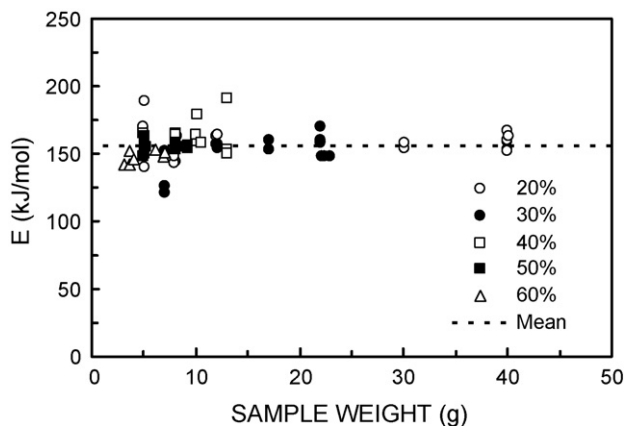


Fig. 3. The relationship between the sample weight and the activation energy. The samples are DTBP/toluene solutions with the concentrations between 20 and 60 wt.%.

controlling by the temperature of the sample vessel wall such as the ARC. Fig. 2 shows an example of the heat rate and the pressure rate of DTBP 40 wt.%/toluene solution. The sample mass is 13.0 g ($\varphi = 3.1$). The heat rate maximum is 227 K/min.

3.2. Decomposition kinetics

Relationship between the activation energy and the DTBP concentration is shown in Fig. 3. Relationship between the frequency factor and the DTBP concentration is shown in Fig. 4. Horizontal dot lines in Figs. 3 and 4 show the average values. The averaged activation energy and the frequency factor were 156.46 kJ/mol and 15.78 s^{-1} . The kinetic plot in the decomposition of DTBP/toluene solution shows the reaction number can be regarded as the first-order of the overall reaction in all of the concentrations because the fitting curves are straight. The $(-\log(k))$ data are not on the fitting line near the onset and the end of reaction. The corresponded temperature range is excluded when the activation energy and the frequency factor are obtained.

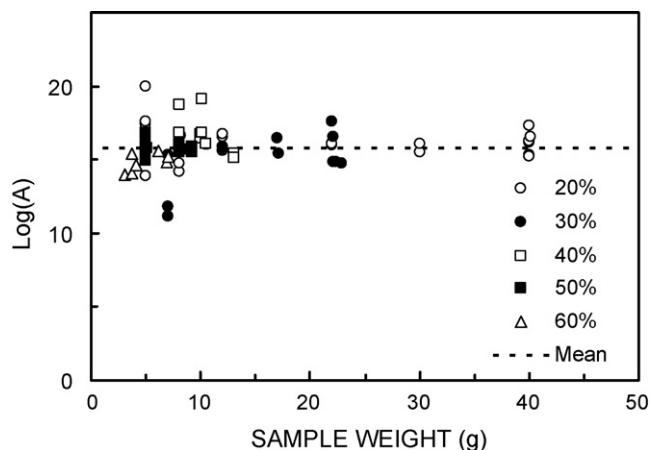


Fig. 4. The relationship between the sample weight and the frequency factor. The samples are DTBP/toluene solutions with the concentrations between 20 and 60 wt.%.

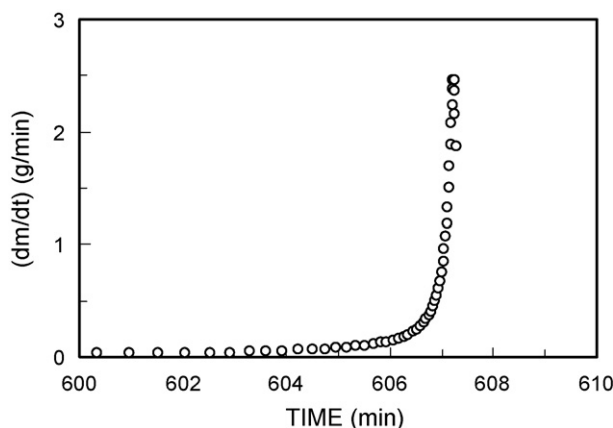


Fig. 5. The example of the time history of the mass loss rate calculated by the measurement data of the APTAC. The sample is DTBP 40 wt.%/toluene solution with the sample mass of 13.0 g.

The activation energy and the frequency factor are nearly the same as the literature values. E and $\log(A)$ in the literature are 155.64 kJ/mol and 15.62 s^{-1} , respectively [7]. E and A are close to the literature values. This result shows the experimental method and the data analysis is appropriate in the measurement of the APTAC. E and A are nearly the constant for the DTBP concentrations. This result shows the reaction process does not vary in the different DTBP concentrations.

3.3. Pressure and gas production

The example of the time history of the mass loss rate calculated using the measurement data of the APTAC is shown in Fig. 5. The time at the maximum mass loss rate closed to the time at the maximum temperature. The time difference between the maximum mass loss rate and the maximum gas production rate is less than about 0.3 s when the DTBP concentration is more than 30 wt.% and the weight is more than 5 g. There is the tendency the time difference is large in the case of the samples with the small amount of DTBP in the DTBP 20 wt.%/toluene solution.

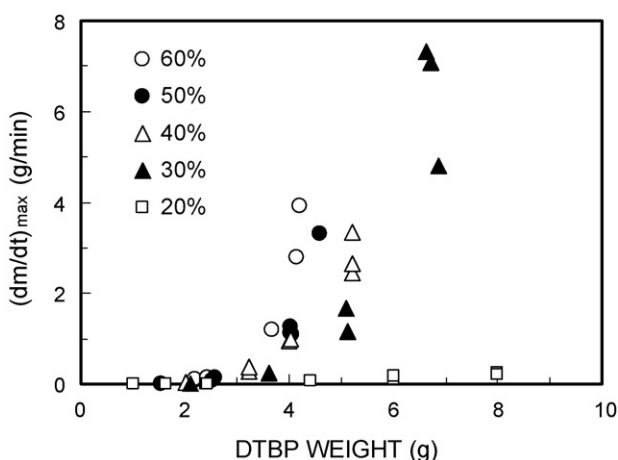


Fig. 6. The relationship between $(dm/dt)_{\max}$ and DTBP weight in toluene in various concentrations of DTBP.

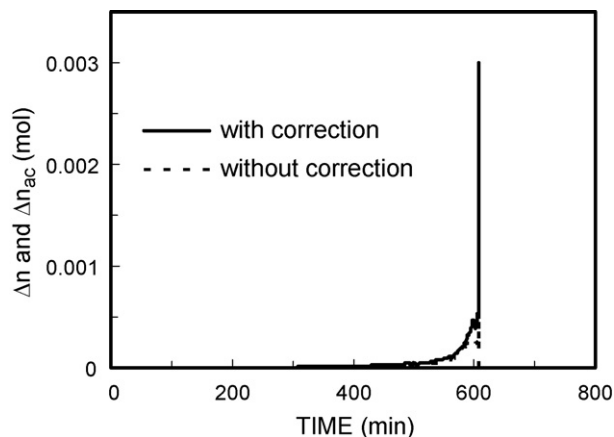


Fig. 7. The time history of the gas production with and without the vapor correction of DTBP and toluene in the vapor–liquid equilibrium. The sample is DTBP 40 wt.%/toluene with 13.0 g of sample weight.

The relationship between the maximum mass loss rate $((dm/dt)_{\max})$ and the DTBP weight in the DTBP/toluene solution is shown in Fig. 6. The $(dm/dt)_{\max}$ value increases exponentially for the DTBP weight. The $(dm/dt)_{\max}$ value increases drastically when the DTBP weight in DTBP/toluene solution is beyond 3 g excluding the case of the sample of 20 wt.%. The $(dm/dt)_{\max}$ value increases with the increase of the DTBP concentration when the DTBP weight is more than 3 g.

The time history of the noncondensable decomposition gas production (Δn and Δn_{ac}) with and without the vapor correction of DTBP and toluene in the vapor–liquid equilibrium. The sample is DTBP 40 wt.%/toluene with 13.0 g of sample weight. The correction means the vapor correction in the vapor–liquid equilibrium in Fig. 7. The moving averages over 10 points before and after the certain point are drawn to smooth the line in the time history. T_{onset} and T_{max} become the each averaged value as the calculation results of the moving average when the moving averages are calculated. There is the same tendency with Δn and Δn_{ac} of the vapor correction and without the vapor correction. A subscript of ac expresses the vapor pressure correction. The

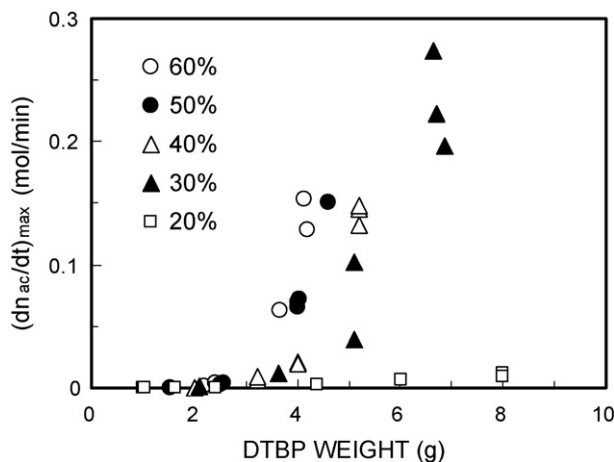


Fig. 8. The relationship between $(dn_{ac}/dt)_{\max}$ and DTBP weight in toluene in various concentrations of DTBP. The $(dn_{ac}/dt)_{\max}$ value is calculated by the vapor pressure correction of DTBP and toluene in the vapor–liquid equilibrium.

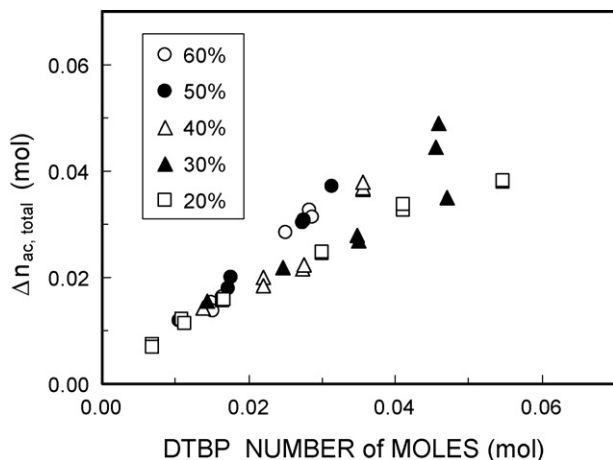


Fig. 9. The relationship between $\Delta n_{ac,total}$ and number of moles of DTBP in toluene in various concentration of DTBP. The $\Delta n_{ac,total}$ values are calculated by the vapor pressure correction of DTBP and toluene in the vapor–liquid equilibrium.

decomposition gas occupies the large part in the sample vessel when compared to the vaporization of DTBP and toluene. The gas production increases drastically in the end of the reaction.

The relationship between the maximum gas production rate ($(dn_{ac}/dt)_{max}$) and the DTBP weight in DTBP/toluene solution is shown in Fig. 8. The $(dn_{ac}/dt)_{max}$ value increases exponentially for the DTBP weight. The $(dn_{ac}/dt)_{max}$ value increases drastically when the DTBP weight in DTBP/toluene solution is beyond 3 g excluding the case of the sample of 20 wt.%. The $(dn_{ac}/dt)_{max}$ value increases with the increase of the DTBP concentration when the DTBP weight is more than 3 g. The behavior of $(dn_{ac}/dt)_{max}$ is in the similar manner of the behavior of $(dm/dt)_{max}$ in Fig. 6.

The relationship between $\Delta n_{ac,total}$ and the number of moles of DTBP in DTBP/toluene solution regarding to various DTBP concentrations is shown in Fig. 9. The $\Delta n_{ac,total}$ value increases proportionally to the number of moles of DTBP. This indicates that the DTBP decomposition gas increases in proportional relation to the mass of DTBP in DTBP/toluene solution. This result is consistent with the experimental fact that the decomposition process is the same in various concentrations of DTBP.

$N_{ncg,ac,total}$ shows the mole ratio of the gas production occurred by the decomposition of DTBP to DTBP contained in the sample. $N_{ncg,ac,total}$ is the gas production index which is one of the intrinsic properties such as the activation energy [8,9]. For example, The $\Delta n_{ac,total}$ value of the DTBP/toluene sample is 0.037 mol in DTBP 40 wt.% with 13.0 g. The number of moles of DTBP in the DTBP/toluene sample is 0.036 mol. $N_{ncg,ac,total}$ is calculated to be 1.0 according to Eq. (12) when the DTBP decomposition of 40 wt.% with 13.0 g is measured.

The averaged $N_{ncg,ac,total}$ is 1.0 when all data are calculated. This value indicates DTBP of 1 mol generates the decomposition gas of 1.0 mol in the whole reaction. The averaged $N_{ncg,total}$ is 1.8. The averaged $N_{ncg,total}$ involves the vapor pressure of DTBP and toluene.

The relationship between $N_{ncg,ac,max}$ and the DTBP weight (g) in DTBP/toluene solution is shown in Fig. 10. $N_{ncg,ac,max}$

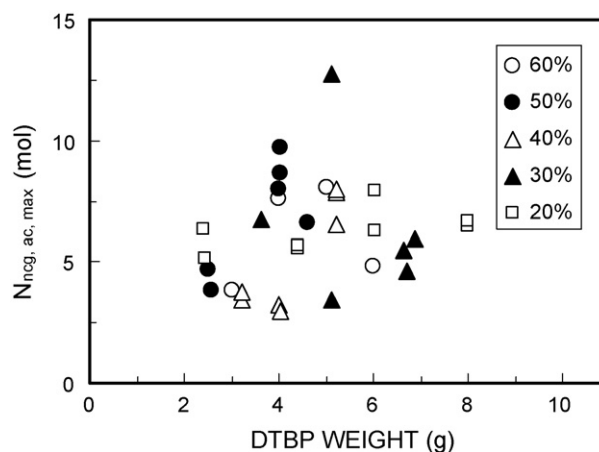


Fig. 10. The relationship between $N_{ncg,ac,max}$ and DTBP weight in toluene in various concentrations of DTBP. The $N_{ncg,ac,max}$ values are calculated by the vapor pressure correction of DTBP and toluene in the vapor–liquid equilibrium.

and $N_{ncg,max}$ are used for evaluating the intensity of the gas production. The DTBP sample of less than 2.3 g in DTBP/toluene solution involved the error because the temperature data varied widely. The dividing the gas production rate by mass loss rate expanded the error in $N_{ncg,ac,max}$. The data of the DTBP sample of less than 2.3 g are deleted in Fig. 10. The $N_{ncg,max}$ values range from 5.7 to 16.2. The $N_{ncg,ac,max}$ values range from 3.0 to 12.8. $N_{ncg,ac,max}$ and $(dn_{ac}/dt)_{max}$ are the corrected values considering the vapor pressure. The intensity of the gas production can be evaluated by $N_{ncg,max}$ and $N_{ncg,ac,max}$. $N_{ncg,max}$ expresses nearer situation to the real gas production than $N_{ncg,ac,max}$ because the vapor pressure effect is considered in $N_{ncg,max}$.

4. Conclusions

The properties of the data obtained by the APTAC were investigated on the basis of the temperature data and the pressure data using DTBP/toluene solution as the sample. The thermal decomposition of DTBP was studied on the basis of the data obtained by the APTAC. The thermodynamics parameters and the gas production were discussed on the basis of the experimental data of various concentrations and weights of DTBP/toluene solution.

The following conclusions are made:

- (1) The activation energy and the frequency factor of DTBP are nearly constant and the same as the literature values in the concentrations between 20 and 60 wt.%. This result suggests the process of the decomposition reaction is the same though the DTBP concentration changes, and the experimental method and the data analysis are appropriate in the measurement of the APTAC.
- (2) The time history of the gas production was evaluated with various weights and concentrations. The DTBP decomposition gas increases in proportional relation to the mass of DTBP in DTBP/toluene solution. This result is consistent with the experimental fact that the decomposition process is the same in various concentrations of DTBP. The total gas

production index, which has the vapor pressure correction, is 1.0 in the decomposition of DTBP. This experimental result indicates DTBP of 1 mol generates the decomposition gas of 1.0 mol in the whole reaction.

References

- [1] S. Chippett, P. Ralbovsky, R. Granville, Proceedings of the International Symposium on Runaway Reaction, Pressure Relief Design and Effluent Handling, 1998, pp. 81–108.
- [2] L. Cisneros, W.J. Rogers, M.S. Mannan, *J. Hazard. Mater.* 82 (2001) 13–24.
- [3] Y. Iwata, H. Koseki, M. Momota, Proceedings of 2003 Asia Pacific Symposium on Safety, 2003, pp. 169–172.
- [4] Y. Iwata, H. Koseki, *J. Sci. Tech. Energetic Mater.* 66 (5) (2005) 375–379.
- [5] C. Yaws, *Chemical Properties Handbook, Physical, Thermodynamic, Environmental, Transport Safety, and Health Related Properties for Organic and inorganic Chemicals*, McGraw-Hill, New York, 1999.
- [6] Y. Iizuka, A. Fujita, K. Akiba, Y. Tomita, *J. Jpn. Soc. Saf. Eng.* 39 (2) (2000) 91–97 (in Japanese).
- [7] A.A. Aldeeb, W.J. Rogers, M.S. Mannan, *Trans. IChemE* 80 (Part B) (2002).
- [8] M.A. Grolmes, M.K. King, *J. Hazard. Mater.* 44 (1995) 253–266.
- [9] M.A. Grolmes, Proceedings of the International Symposium on Runaway Reaction, Pressure Relief Design and Effluent Handling, 1998, pp. 219–245.