Performance evaluation of differential accelerating rate calorimeter for the thermal runaway reaction of di-*tert*-butyl peroxide

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Abstract The thermal behavior of di-*tert*-butyl peroxide (DTBP) has been studied by accelerating rate calorimetry (ARC), in order to obtain a better understanding of novel differential accelerating rate calorimetry (d-ARC) developed by OmniCal Inc. presently. Thermal analysis, kinetic analysis, and estimation of time to maximum rate (TMR_{ad}) of 5–20 mass% DTBP and toluene mixture were performed and compared with the past reports. From the experimental results, moderately hazardous mixture which was evaluated inaccurately by the conventional ARC was analyzed successfully by d-ARC. Kinetic parameters were determined to be 153–164 kJ mol^{-1} of the activation energy and 3.3E+17 to 3.3E+18 min^{-1} of the frequency factor by d-ARC, and agreed with the past reports. Meanwhile, the kinetics of low-concentrated DTBP mixture were calculated to be incorrect value by the conventional ARC. Furthermore, TMR_{ad} of low-concentrated DTBP mixture was successfully estimated by d-ARC, while incorrect estimations were obtained by the conventional ARC. It was concluded that d-ARC has better performance of adiabatic calorimetry and is useful tool of the thermal risk assessment for chemical process safety.

Introduction

A storage tank, one of the essential equipment of chemical processes, has hazards of fire and explosion due to the accumulated heat of self-decomposition of stored chemicals. Recently, some fire and explosion accidents of stored chemicals occurred in Japan. In order to prevent these accidents, it is necessary to evaluate precisely the thermal hazard of chemicals under adiabatic condition. Accelerating rate calorimeter (ARC), developed by Dow Chemical Company in the 1970s, is well known as useful tool for evaluating the thermal runaway hazard of the chemical reaction system under adiabatic condition. ARC is designed so that heat flow between the sample vessel and its surroundings is eliminated by controlling the surrounding temperature to be equal to temperature of the sample vessel. Thus, there is no temperature gradient between the sample vessel and its surroundings, and quasi-adiabatic condition is established.

Recently, an innovative ARC was developed by OmniCal Inc. The novel apparatus is equipped with differential vessels and heat compensation system. OmniCal Inc. promotes that differential vessel type ARC (d-ARC) has better adiabatic control performance than single vessel type ARC (s-ARC), however, only short information is advertised on its web site [1]. Thus, the details on the performance of adiabatic calorimetry are not well understood.

In this study, in order to obtain a better understanding of the thermal hazard evaluation performance of d-ARC,

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thermal analyses using two types of adiabatic calorimetry were carried out. As the test material, di-*tert*-butyl peroxide (DTBP) [(CH$_3$)$_3$COOC(CH$_3$)$_3$] was selected. DTBP is an organic peroxide which has peroxy bond (–O–O–) flanked by two tertiary butyl groups, and widely used as an initiator of polymerization reaction in the chemical industry. Meanwhile, DTBP has unstable nature due to the instability of peroxy bond. For a safety handling, its decomposition behavior has been studied for a long time and some research articles have been published recently [2, 3]. Therefore, DTBP is recommended as the standard sample for checking and evaluating the performance of calorimeter on the thermal hazard analysis [4, 5]. DTBP was considered to be an appropriate test material in this study.

Based on the comparisons of experimental results, kinetics and temperature at which time to maximum rate (TMR$_{ad}$) is 24 h (T_{D24}), performance of d-ARC was discussed.

Principle of differential type accelerating rate calorimetry

When the sample temperature reaches to the initial temperature of exotherm (T_a), heat of decomposition of sample (ΔQ) is released and temperature of sample side rises ΔT_0. The relation of ΔQ and ΔT_0 is expressed as,

$$\Delta Q = (C_v + C_s) \times \Delta T_0. \tag{1}$$

In this equation, C_v and C_s stand for the heat capacity of the calorimetric vessel and sample, respectively. In order to equalize temperature of the sample vessel and reference vessel, reference vessel should be heated up by following heat (ΔQ_{comp}),

$$\Delta Q_{comp} = C_v \times \Delta T_0. \tag{2}$$

However, ΔQ_{comp} also equals the decomposition heat consumed for the sample vessel. Accordingly, the sample side is made into containerless condition by adding the heat of ΔQ_{comp} ("containerless condition" means that heat of decomposition is consumed for only temperature rise of sample, thus, it can be considered that the sample is in quasi-adiabatic condition.). In the next process, supplying ΔQ_{comp} as compensation heat to both vessels, then, temperature of the sample vessel rises ΔT_1. Relationship between ΔQ_{comp} and ΔT_1 is as follows:

$$\Delta Q_{comp} = (C_v + C_s) \times \Delta T_1 = C_v \times \Delta T_0. \tag{3}$$

Repeating this compensation process for controlling to minimize the difference of temperature between the sample side and the reference side, where k is given as number of times of compensation, ΔT_k and ΔT_0 is expressed as follows:

$$\Delta T_1 = \frac{C_v}{C_v + C_s} \times \Delta T_0,$$

$$\Delta T_2 = \frac{C_v}{C_v + C_s} \times \Delta T_1 = \left(\frac{C_v}{C_v + C_s}\right)^2 \times \Delta T_0,$$

$$\vdots \tag{4}$$

$$\Delta T_k = \left(\frac{C_v}{C_v + C_s}\right)^k \times \Delta T_0.$$

Summation of ΔT_k is shown as follows:

$$\sum_{k=0}^{n} \Delta T_k = \frac{\Delta T_0 \left\{ 1 - \left(\frac{C_v}{C_v+C_s}\right)^n \right\}}{1 - \left(\frac{C_v}{C_v+C_s}\right)}. \tag{5}$$

Defining thermal inertia φ as $\left(\frac{C_v+C_s}{C_s}\right)$, following equation is obtained:

$$1 - \left(\frac{C_v}{C_v + C_s}\right) = \frac{1}{\varphi}. \tag{6}$$

Hence, summation of ΔT_k is

$$\sum_{k=0}^{n} \Delta T_k = \Delta T_0 \times \frac{1 - \left(\frac{C_v}{C_v+C_s}\right)^n}{\frac{1}{\varphi}}$$
$$= \varphi \times \Delta T_0 \times \left\{ 1 - \left(\frac{C_v}{C_v + C_s}\right)^n \right\}. \tag{7}$$

Since C_v and C_s is larger than zero, ($C_v + C_s$) is larger than C_v, and $\lim_{n\to\infty} \left(\frac{C_v}{C_v+C_s}\right)^n$ converges to zero. Thus, by repeating compensation, the summation of ΔT_k converges as follows:

$$\sum_{k=0}^{n} \Delta T_k = \varphi \times \Delta T_0. \tag{8}$$

Temperature rise in adiabatic condition is given by $T_a + \varphi \Delta T_0$.

In s-ARC measurement, adiabatic condition is established by minimizing the temperature difference between the sample vessel and surrounding temperature. Since it is unavoidable that a part of the heat released by the sample serves to heat the sample vessel, the sample temperature of s-ARC test does not reach $T_a + \varphi \Delta T_0$ actually, and φ-correction, a correction for the thermal inertia of the vessel, has to be carried out. In addition, since the changes of reaction progress or temperature definitely accompany the change of specific heat capacity of sample or sample container, φ-factor is not constant value and varies as a function of temperature or reaction progress. Nevertheless, φ-correction is generally performed based on the premise of constant φ-factor.

Meanwhile, in d-ARC measurement, no consideration for change of specific heat capacity is required by

differential system and compensation technique. Consequently, the sample temperature really reaches $T_a + \varphi \Delta T_0$ without any correction. It is revolutionary point of d-ARC.

Experimental

Materials

Materials used in this study were DTBP of Sigma Aldrich Co. LLC. and toluene of Tokyo Chemical Industry Co., LTD.. Both reagents were used without further purification. As the test samples, 20, 15, 10, and 5 mass% of DTBP with toluene mixtures were prepared.

Methods

The thermal tests of DTBP under adiabatic condition were carried out by using two types of ARC, and schematic drawings of s-ARC, and d-ARC are shown in Fig. 1. ARCs employed in this study were DARC^{TM} of OmniCal Inc. as d-ARC and Euro-ARC of Thermal Hazard Technology as s-ARC, respectively, [1, 6].

As the sample vessel shown in Fig. 2, spherical vessel for s-ARC and cylindrical vessel for d-ARC were used. Both the sample vessels were made from Hastelloy-C. In s-ARC, the vessel, in which 5 g of DTBP mixture was injected, was connected to the lid of heating oven and tests were started. In d-ARC, the sample vessel, which contains 5 g DTBP mixture, was set at sample side and empty vessel was set at reference side, and the test was started. Both the adiabatic measurements, initial temperature were set at 303 K. Wait time and temperature step of Heat–Wait–Search (H–W–S) for s-ARC and Heat–Soak–Search (H–S–S) for d-ARC were 15 min and 5 K. The threshold of self heat rate to switch from H–W–S and H–S–S mode to adiabatic control mode was 0.02 K min^{-1}.
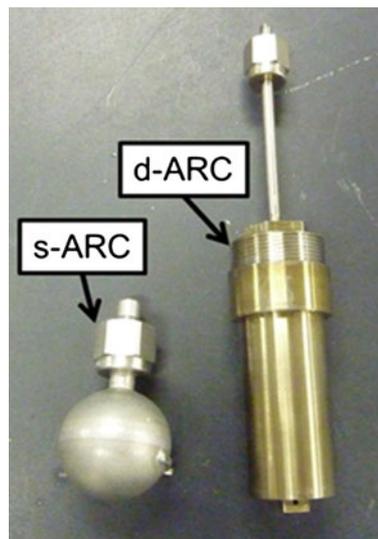

Fig. 2 Appearance of the sample vessels

Result and discussion

Comparison of the thermal behavior of DTBP mixtures by d-ARC with that by s-ARC

Figure 3 shows the thermal behavior of 20 mass% DTBP solution. Comparing the raw data of d-ARC with that of s-ARC, d-ARC showed a steeper temperature rise, and time from start temperature of thermal reaction to temperature at maximum self heat rate was shorter than s-ARC. The self heat rate (1st derivation of temperature curve) of two types of ARC is shown in Fig. 4. In d-ARC, maximum self heat rate reached 67.2 K min^{-1}, while 6 K min^{-1} was shown by s-ARC. Thermal test results are summarized in Table 1. Since all of the decomposition heat is consumed for only temperature rise of the sample in d-ARC, adiabatic measurement of DTBP by d-ARC showed much violent behavior than s-ARC.

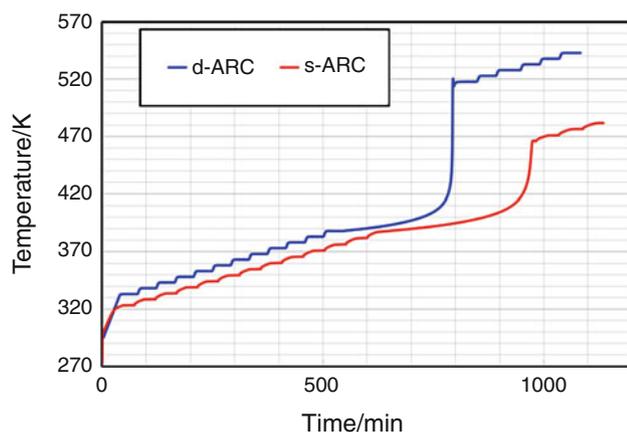**Fig. 1** Schematic drawings of accelerating rate calorimeter: **a** s-ARC, **b** d-ARC
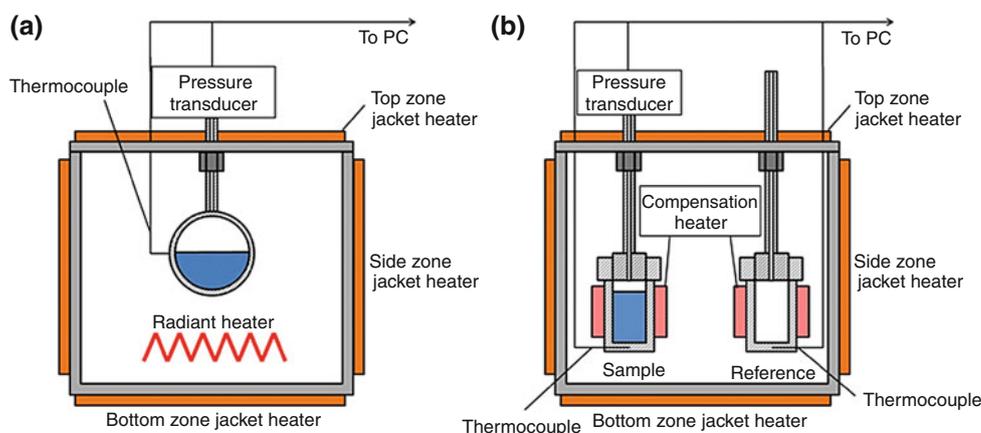
Fig. 3 Results of thermal behavior of 20 mass% of DTBP mixture measured by two types of ARC
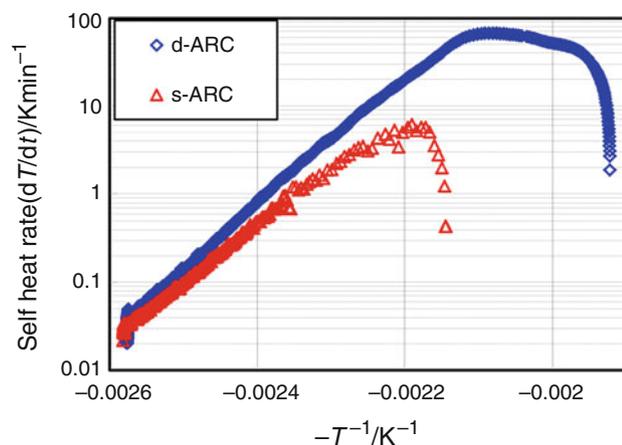

Fig. 4 Comparison of self heat rate of 20 mass% DTBP mixture

Meanwhile, concerning the results of 5–15 mass% DTBP mixtures, the start temperature of thermal reaction measured by s-ARC was higher than that of d-ARC. In the results of s-ARC, since the self heat rate which is diluted by the heat capacity of sample container did not surpass the criteria of adiabatic control, the start temperature of thermal reaction must be higher than true value, and the reactive components were consumed uselessly. Consequently, even though the φ-correction was performed, the adiabatic temperature rise

(heat of decomposition) was smaller than that by d-ARC in conditions of 5 and 10 mass% of DTBP mixtures. According to Stoessel [7], typical energy of desired synthesis reaction is 100 kJ kg^{-1} ($\Delta T_{ad} = 50$ K), and 5–10 mass% DTBP mixtures have the same level of thermal hazard. Thus, it is likely that the incorrect results are obtained by s-ARC for the moderate reaction system such as typical desired synthesis reaction.

From these results, it was found that d-ARC has high sensitivity and adiabatic control performance, and gives a good experimental result on the thermal analyses of chemicals under adiabatic condition.

Kinetic analysis and φ-correction of ARC data

In accelerating rate calorimetry, adiabatic kinetic parameters of n-th order reaction are given by the following equation [8]:

$$\frac{dT}{dt} = A \cdot \left(\frac{T_f - T}{\Delta T}\right)^n \cdot \Delta T \cdot c_0^{n-1} \exp\left(-\frac{E}{RT}\right). \quad (9)$$

Where T, t, A, T_f, ΔT, c_0, n, E, and R are temperature, time, frequency factor, temperature at exotherm finished, adiabatic temperature rise, initial concentration of chemicals, reaction order, activation energy, and gas constant, respectively. Defining $k*$ as

$$k* = \frac{dT}{dt} \cdot \left(\frac{\Delta T}{T_f - T}\right)^n \cdot \Delta T^{-1}, \quad (10)$$

following Eq. 11 is obtained:

$$\ln k* = \ln A \cdot c_0^{n-1} - \frac{E}{RT}. \quad (11)$$

Hence, kinetic parameters E and A are given by slope and intercept of $1/T$ versus $\ln k*$ plot (Arrhenius plot) as shown in Fig. 5. According to Batt and Benson, it was reported that the thermal decomposition of DTBP progressed in 1st order [9]. In the 20 mass% DTBP solution, activation energies were calculated as 157 kJ mol^{-1} with d-ARC and 156 kJ mol^{-1} with s-ARC, and frequency factors were 3.3E + 17 min^{-1} of d-ARC and 2.7E + 17 min^{-1} of s-ARC. Experimental kinetic parameters of DTBP solutions are summarized in Table 2.

Table 1 Summary of thermal analysis by d-ARC and s-ARC

Conc. of DTBP/mass%	Adiabatic temperature rise ΔT/K		Start temperature of thermal reaction T_a/K		Maximum Self heat rate dT/dt_{max}/K min^{-1}	
	s-ARC[a]	d-ARC	s-ARC	d-ARC	s-ARC	d-ARC
5	5.6 (9.5)	27.1	408	398.2	0.03	0.88
10	25.6 (42.7)	62.1	399.5	393.2	0.09	1.61
15	50.4 (85.4)	93.6	399.2	388.2	1.25	16.7
20	79.0 (130.3)	132.1	387.3	388.2	6.13	67.2

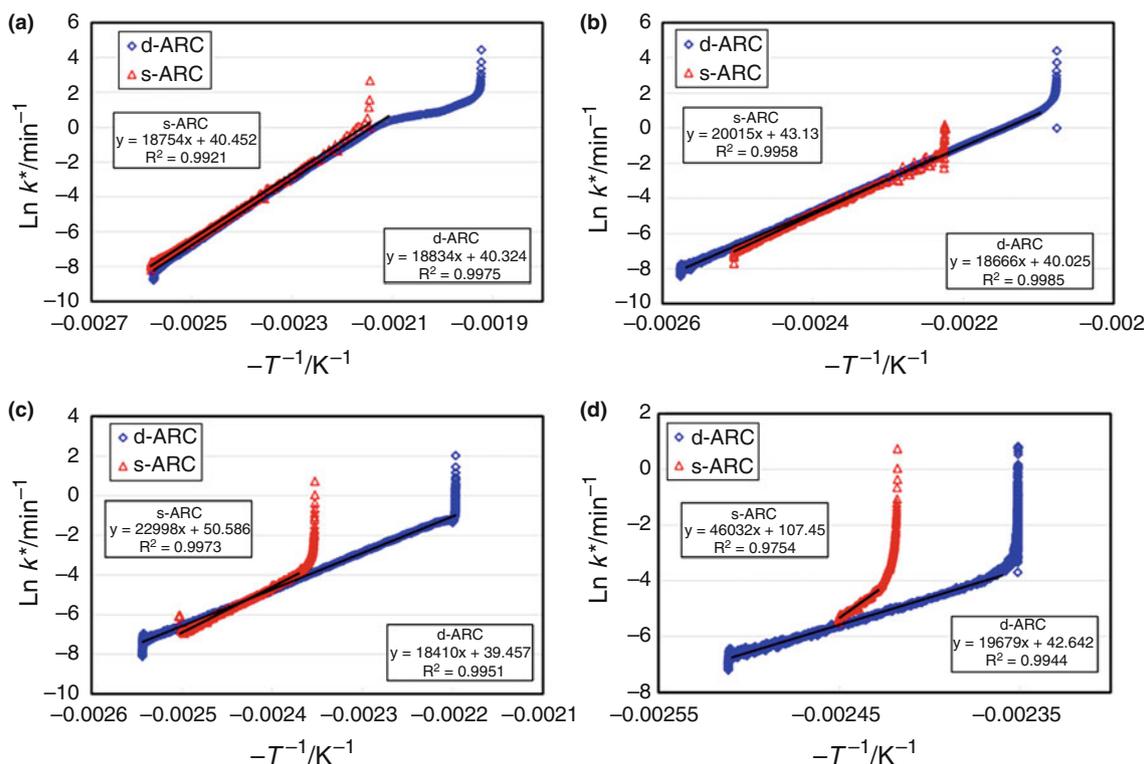[a] φ-corrected adiabatic temperature rise in brackets

Fig. 5 Arrhenius plots of the thermal reaction of DTBP and toluene mixtures: **a** 20 mass% DTBP, **b** 15 mass% DTBP, **c** 10 mass% DTBP, and **d** 5 mass% DTBP

Table 2 Summary of kinetic parameters of DTBP thermal reaction

Conc. of DTBP/mass%	Activation energy E/kJ mol^{-1}		Frequency factor A/min^{-1}	
	s-ARC	d-ARC	s-ARC	d-ARC
5	383	164	4.6E + 46	3.3E + 18
10	191	153	9.3E + 21	1.4E + 17
15	166	155	5.4E + 18	2.4E + 17
20	156	157	2.7E + 17	3.3E + 17

According to the past report, kinetics of thermal reaction of 7.5–20 mass% DTBP in toluene were determined as 157 kJ mol^{-1} of activation energy and 2.0E + 18 min^{-1} of frequency factor [10]. Furthermore, a Round-robin study on the decomposition reaction of 15 mass% of DTBP in toluene using various adiabatic equipments [ARC, Phi-Tec, Pressure Dewar calorimeter (Dewar), temperature controlled reactor (CRVM), and the Automatic Pressure Track Accelerating Calorimeter (APTAC)] reported by Kersten et al. [11], the activation energy and frequency factor were 154.5–161.8 kJ mol^{-1} and 2.0E + 17–2.0E + 18 min^{-1}, respectively. In d-ARC test, kinetic parameters agreed with the report. On the other hands, regarding the s-ARC, only 20 and 15 mass% of DTBP showed a good agreement with the reports.

In regard to s-ARC, since decomposition heat is consumed for the temperature rise of both sample and its container, a correction for the thermal inertia of the container (called φ-correction) is required. φ-Corrected self heat rate is given by the following equations [8]:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = A \cdot (T_a + \varphi \cdot \Delta T - T) \cdot \exp\left(-\frac{E}{RT}\right), \tag{12}$$

$$\varphi = \left(\frac{C_v + C_s}{C_s}\right). \tag{13}$$

where C_s and C_v mean the heat capacity of sample and vessel, and φ is called as thermal inertia or adiabaticity coefficient. Figure 6 shows the comparisons of ARC curves of d-ARC with φ-corrected s-ARC. 15 and 20 mass% of DTBP mixtures showed a good agreement, but 5 and 10 mass% of DTBP mixtures were disagreed. Since 5 and 10 mass% DTBP mixtures have much moderate thermal reactivity than 15 and 20 mass% DTBP mixtures, thermal dilution effect has a strong influence on the thermal sensitivity of ARC test.

Concerning the raw data of 5 mass% of DTBP mixture by s-ARC, dT/dt were 0.010–0.014 K min^{-1} during two steps at temperature below T_a and 0.02–0.03 K min^{-1} at temperature from T_a to T_f. These values were near the threshold of self heat rate to switch from adiabatic control mode to HWS mode (0.02 K min^{-1}). In s-ARC measurement, since ΔT measured by s-ARC was lower than that by
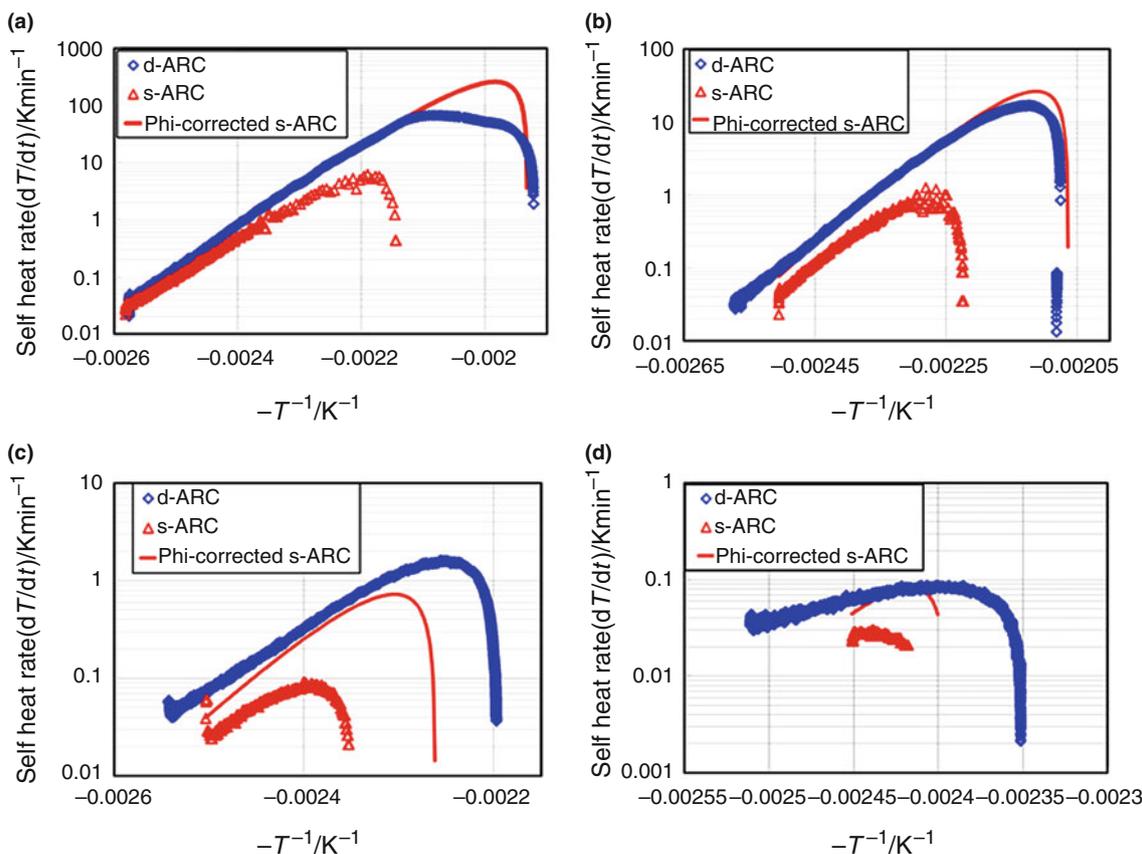
Fig. 6 Comparisons of experimental ARC curves with φ-corrected s-ARC curves: **a** 20 mass% DTBP, **b** 15 mass% DTBP, **c** 10 mass% DTBP, and **d** 5 mass% DTBP

d-ARC, thermal profiles at temperature below T_a which must be measured essentially were not obtained. Hence, adiabatic temperature curve of 5 mass% of DTBP was measured inadequately and incorrect kinetic parameters were estimated by s-ARC. Even though the φ-correction was performed, incorrect adiabatic temperature curves were also drawn by incorrect kinetic parameters.

From these results and analysis, it was found that adiabatic kinetics of thermal reaction of chemicals including moderate hazardous reaction, such as decomposition of low-concentrated DTBP mixture, were assessed correctly by d-ARC.

Evaluation of T_{D24} for chemical process safety

TMR_{ad}, the time of the thermal explosion takes to develop under adiabatic condition, is an important index for chemical process safety expressed as following equation [8]:

$$TMR_{ad} \approx \frac{RT^2}{E \cdot \left(\frac{dT}{dt}\right)}. \tag{14}$$

T_{D24} was determined as temperature at which TMR_{ad} equals 1,440 min by calculating Eq. 14. Table 3 shows the summary of T_{D24} estimation. According to the past study,

T_{D24} calculated by kinetic simulation of the experimental data of differential scanning calorimeter (DSC) were reported as shown in fourth column of Table 3 [12]. Comparing experimental data with the simulations, T_{D24} of d-ARC showed a good agreement with DSC simulations.

Regarding to the 5 mass% DTBP mixture, T_{D24} was determined to be 394.8 K by s-ARC which was 14 K higher than that of d-ARC, and it means 348.9 min of TMR_{ad} by d-ARC. Accordingly, T_{D24} of 5 mass% of DTBP mixture by s-ARC was approximately 1,100 min shorter than that of d-ARC as shown in Fig. 7. Adopting this value of T_{D24} as the index of process safety management, the chemical process will lead to hazardous situation. The thermal hazard of 5 mass% DTBP mixture is categorized as "desired synthesis reaction" as described in Stoessel [7]. Evaluating such moderate hazardous reactions by s-ARC, it is likely that an incorrect process safety indicator is obtained.

From these evaluations and discussions, it was concluded that the thermal behavior and kinetic parameters of DTBP decomposition were not correctly evaluated by s-ARC due to the limitation of thermal sensitivity in case of the measurement of low-concentrated DTBP mixture. Thus, the estimation of T_{D24} by s-ARC showed an incorrect

Table 3 Summary of T_{D24} of DTBP thermal reaction

Conc. of DTBP/mass%	Temperature at TMR$_{ad}$ = 24 h T_{D24}/K		
	s-ARC	d-ARC	Simulation [12]
5	394.8	380.5	380.3
10	383.1	375.1	374.4
15	377.2	373.5	371.1
20	372.5	372.2	368.6
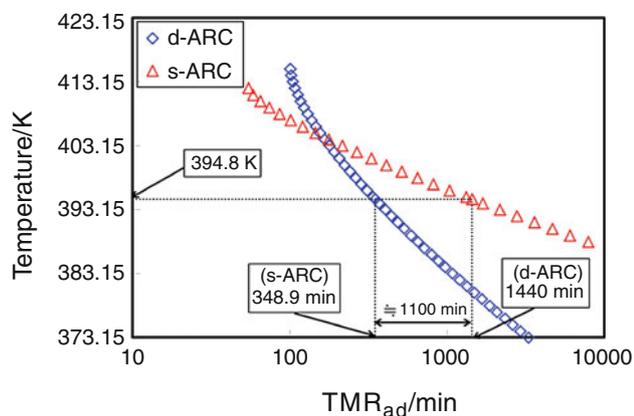
Fig. 7 Comparisons of TMR$_{ad}$ curves of 5 mass% DTBP and toluene mixture

value. On the other hand, T_{D24} obtained by d-ARC showed a good agreement with the past report, and d-ARC is useful for the process safety assessment on the moderate reaction system.

Conclusions

From the results of ARC experiments, kinetic analysis and estimation of TMR$_{ad}$ of DTBP/toluene mixture, following conclusions can be drawn:

1. d-ARC has high sensitivity and adiabatic control performance, and gives a good experimental result of thermal analysis of chemicals under adiabatic condition.
2. Experimental kinetic parameters were determined to be 153–164 kJ mol^{-1} of activation energy and 3.3E + 17–3.3E + 18 min^{-1} of frequency factor by d-ARC, and agreed with past reports. Meanwhile, incorrect kinetics of 10 and 5 mass% of DTBP mixtures were given by s-ARC due to the thermal dilution effect.
3. Adiabatic kinetics of thermal reaction of chemicals including slight hazardous reaction, such as decomposition of low-concentrated DTBP mixture, were assessed correctly by d-ARC.
4. Correct kinetic parameters obtained by d-ARC gave the correct process safety indicator. Meanwhile, wrong process safety indicator was given by incorrect kinetics obtained by s-ARC.
5. Compared with the conventional ARC, d-ARC has better performance of adiabatic calorimetry, and is useful tool for evaluating the thermal hazard of chemical reactions.

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