

# Derivation of the self-accelerating decomposition temperature for self-reactive substances using isothermal calorimetry

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## Abstract

In order to determine the self-accelerating decomposition temperature (SADT) for self-reactive substances in packaging, it is proposed that chemical kinetic parameters are derived from the data obtained by an isothermal heat flux reaction calorimeter (C80D), after which the SADT is evaluated from theoretical equations based on the Semenov model. This method avoids the shortcomings of the US isothermal storage test and the Dewar vessel heat accumulation storage test. We have evaluated the SADTs for a dozen self-reactive substances. These SADTs coincide well with the US SADT test results and have an excellent correlation with the Dewar vessel test results. This proposed method gives more accurate results than the SADT-estimating method using data obtained by an accelerating rate calorimeter.

*Keywords:* Decomposition; Calorimetry; Self-reactive; Self-accelerating; Semenov model

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## 1. Introduction

A self-accelerating decomposition temperature (SADT) is defined in the United Nations' Recommendation as the lowest temperature at which self-accelerating decomposition may occur in an organic peroxide or self-reactive substance in the packaging for transportation purposes [1, 2]. The SADT determines whether the substance should be subject to temperature control during transport. The United Nations committee recommends four test methods for the determination of the SADT, involving a storage test either at a fixed external temperature or under near-adiabatic conditions [2]. The test method selected should be such that it is appropriate for the size

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and material of the actual package, as the SADT varies according to package size and material. However, there are serious disadvantages in performing these tests [3, 4]. Firstly, it takes a long time for these tests to determine the SADT. The US SADT test and the Dewar vessel heat accumulation storage test require a minimum waiting period of 7 days in the absence of self-heating. Secondly, sample sizes are so high, varying between 400 g and 200 kg, that danger might appear in a test by some chance. Thirdly, before conducting the test, it is necessary to prepare a special test facility which has a protective enclosure and is equipped with an apparatus for the disposal of exhausted wastes.

Therefore, Wilberforce [3] proposed a method for estimation of the SADT using an accelerating rate calorimeter (ARC) in order to avoid the drawbacks mentioned above. Fisher and Goetz [4, 5] have since applied this method to a variety of self-reactive substances and have advanced its usage capabilities. Mores et al. [6] also independently submitted a method for the determination of SADTs, analyzing ARC data based on the Semenov, the Frank–Kamenetskii and the Thomas models. However, the limited accuracy of SADTs estimated by using ARC data, owing to its  $0.02\text{ }^{\circ}\text{C min}^{-1}$  thermal sensitivity, has been pointed out, which has resulted in the adoption of the wide safety margins to cover irregularities produced by changes in kinetic mechanism, autocatalysis, phase change, evaporation and so on, by Whitmore and Wilberforce [7]. Accordingly, they compensated for errors which arise in extrapolating ARC data to the lower temperatures around the SADT by introducing a thermal activity monitor (TAM) [7]. On the other hand, Kotoyori [8, 9] proposed another method for determining SADTs using kinetic data obtained at slightly higher temperatures than the SADT, using an adiabatic self-ignition testing apparatus (SIT).

In this study, we determine the chemical kinetic parameters of a dozen self-reactive substances at the temperatures covering their own SADTs, using an isothermal heat flux reaction calorimeter (C80D), and we estimate the SADTs for them using these kinetic parameters, based on the Semenov model. The SADTs obtained by this method are compared to those by other testing and semi-theoretical methods and the advantages of this methodology are discussed.

## 2. Principle theory of calculation

### 2.1. Derivation of chemical kinetic parameters

The rate expression for the consumption of reactant is defined as

$$-\frac{dM}{dt} = AM^n \exp(-E/RT). \quad (1)$$

The  $\exp(-E/RT) \ll \exp(-E/RT_{\text{DSC}})$  appears when  $T < T_{\text{DSC}}$ , so we can assume  $M$  is equal to  $M_0$  because reactant consumption is close to zero. Therefore, the heat flow of reaction is as follows:

$$M \frac{dH}{dt} = \Delta H AM_0^n \exp(-E/RT). \quad (2)$$

Taking the natural logarithms of both sides of Eq. (2), we obtain Eq. (3):

$$\ln\left(M \frac{dH}{dt}\right) = \ln(\Delta H A) + n \ln M_0 - \frac{E}{RT} \quad (3)$$

$$= a_1 - \frac{E}{RT} \quad (3')$$

$$= a_2 + n \ln M_0, \quad (3'')$$

$$a_1 = \ln(\Delta H A) + n \ln M_0, \quad (4)$$

$$a_2 = \ln(\Delta H A) - \frac{E}{RT}. \quad (5)$$

Plotting the heat flow values measured at each temperature in a constant mass ( $M_0$ ) by isothermal calorimetry on a graph of logarithms of heat flow ( $\ln(M dH/dt)$ ) versus inverse temperature ( $1/T$ ), we can easily calculate the activation energy ( $E$ ) from the slope of an empirical equation corresponding to Eq. (3)'. Then, plotting the other heat flow values, varying the mass ( $M_0$ ) on a log scale diagram of heat flow ( $M dH/dt$ ) versus mass ( $M_0$ ), we can also obtain an order of reaction ( $n$ ), corresponding to Eq. (3)''. Consequently, the product of  $\Delta H$  and  $A$  can be calculated by using Eq. (5) from the activation energy ( $E$ ), the order of reaction ( $n$ ) and an intercept ( $a_2$ ) of the straight line equation (3)'.

## 2.2. Semenov model

According to the Semenov model, the rate of the uniform temperature rise in a system is established by the difference between the rate of heat generation for the system and the rate of heat transfer to the environment by the following equation:

$$C_p M_0 \frac{dT}{dt} = \Delta H M_0^n A \exp(-E/RT) - US(T - T_0). \quad (6)$$

Further, at the temperature of no return ( $T_{NR}$ ), both  $dT/dt = 0$  and  $d(dT/dt)/dT = 0$  exit. Therefore, Eq. (6) can be expressed by Eqs. (7) and (8):

$$B_1 \exp(-E/RT_{NR}) - B_2(T_{NR} - T_0) = 0, \quad (7)$$

$$\frac{B_1 E}{RT_{NR}^2} \exp(-E/RT_{NR}) - B_2 = 0, \quad (8)$$

where

$$B_1 = \Delta H A M_0^{n-1} / C_p \quad \text{and} \quad B_2 = US / (C_p M_0).$$

Putting Eq. (8) in order, the following equation is given:

$$\frac{E}{RT_{NR}} - 2 \ln\left(\frac{1}{T_{NR}}\right) + \ln\left(\frac{USR}{M_0^n \Delta H A E}\right) = 0. \quad (9)$$

We can solve question (9) for its root  $T_{NR}$  by numerical calculation. Moreover, Eqs. (7) and (8), with  $B_1$  and  $B_2$  eliminated, are combined into one equation as

$$E/R = T_{NR}^2 / (T_{NR} - T_0). \quad (10)$$

When the conditions of Eqs. (7) and (8) are obtained, the temperature of the surroundings ( $T_0$ ) must be equal to the SADT ( $T_{SADT}$ ), i.e.,

$$T_{SADT} \equiv T_0 = T_{NR} - \left( \frac{RT_{NR}^2}{E} \right). \quad (11)$$

### 3. Experiment

#### 3.1. Measuring apparatus

For this experiment, an isothermal heat flux reaction calorimeter (C80D) manufactured by SETARAM in France was used. The procedure of measurement is as follows. A test sample is placed in an experimental vessel with a removable volume of 15 ml functioning as a heat sink. The temperature of the block including this vessel is maintained at a constant temperature. The heat flux detector connecting the vessel thermally to the block emits a signal which is proportional to the heat per unit time exchanged between the vessel and the block. Therefore, the calorimeter monitors the heat flux between the sample under investigation and the block. The heat flux detector integrates all thermal exchanges occurring as physical chemistry processes. The calorimeter has two identical vessels placed side by side in two cavities machined in the calorimetric block, and signals from both heat flux detectors are connected in opposition so that the compensation for parasitic phenomena can be made, i.e. a differential arrangement. The C80D has the following general specifications: temperature ranges are ambient to 300 °C, a heat flux detection limit of 10  $\mu$ W, an approximate time constant with a full experimental vessel of 250 s and a detection limit in instant energy of 1 mJ.

The C80D can be provided with various other applicable functions, but in this paper it was used as an isothermal heat flux calorimeter with high detection sensitivity.

#### 3.2. Procedure and conditions

Using the C80D, monitoring was carried out for a period of about 200 min at constant temperatures and scanned at the several temperatures every 5 to 10 °C. Temperatures in the 15–50 °C range were set at 30–100 °C lower than the onset temperature measured by a conventional type of differential scanning calorimeter set with a sealed cell (SC-DSC), so as to include the SADT of the test sample [11]. Samples ranging from 2 to 15 g in mass were tested.

Typical examples of data obtained by the C80D are shown in Figs. 1–3, which illustrate the simultaneous records of heat flow and temperature with time. Generally it takes 100 min or less for the measurements to reach a steady state in both

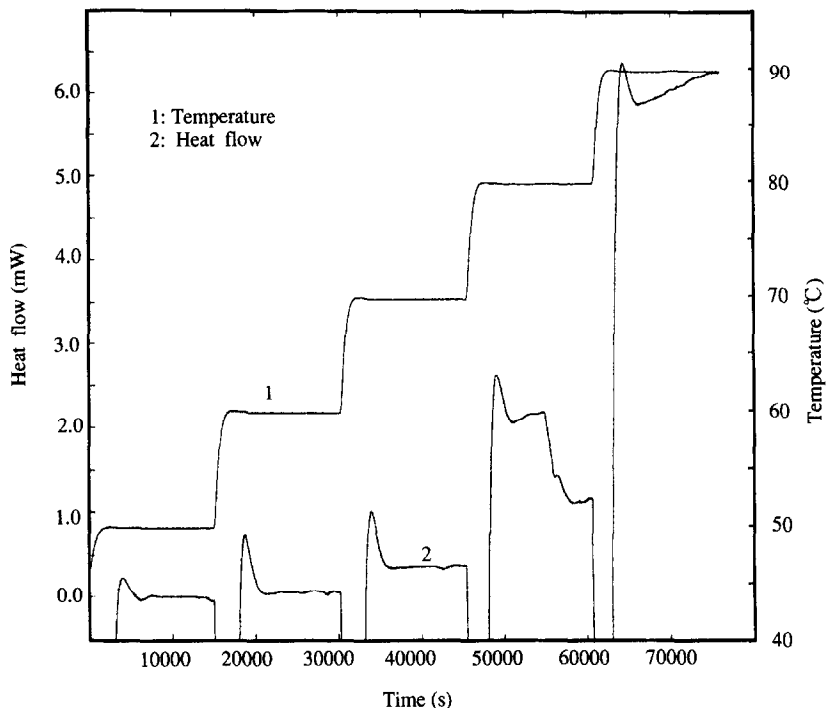


Fig. 1. Reaction heat flow at each temperature step versus time for BPD.

observations at each step. Some irregularities can be seen in heat flow measurements. The chemical kinetic parameters were derived according to Section 2.1.

For example, a sample vessel was filled with a 11.2671 g sample of cumene hydroperoxide (CHP) and both heat flow and temperature were simultaneously measured under isothermal conditions at four steps every 10 °C in the 50–80 °C temperature range. Figs. 4 and 5 are typical examples, in which the data are plotted. The values of  $1.137 \times 10^4$  K for  $E/R$  and 1.02 for the order of reaction ( $n$ ) were determined from the slopes of the straight lines for the heat flow using the least-squares method, in Fig. 4 varying the temperature and in Fig. 5 varying the sample masses. The value of  $23.70 \ln(W/g^n)$  for  $\ln(\Delta H A)$  was calculated from the intercepts of the straight lines ( $a_1$ ) and ( $a_2$ ).

When the sample mass was not changed, the values of  $E/R$  and  $\ln(\Delta H A)$  were derived from a pair of recorded data of heat flow and temperature assuming  $n = 1.0$ .

In accordance with Section 2.2, the SADTs for a 25 kg package were calculated using a wetted area,  $S = 4812.4 \text{ cm}^2$ , and an overall heat transfer coefficient,  $U = 2.8386 \times 10^{-4} \text{ J cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$ , cited from [4]. The SADTs for a 0.51 Dewar vessel were also carried out with  $S = 303 \text{ cm}^2$  and  $U = 1.4567 \times 10^{-4} \text{ J cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$ , cited from [9]. The SADTs, 79 °C for the 25 kg package and 88 °C for the 0.51 Dewar vessel containing CHP for example, were calculated from Eq. (11), following determination of the temperature of no return,  $T_{\text{NR}} = 90 \text{ °C}$  and 100 °C

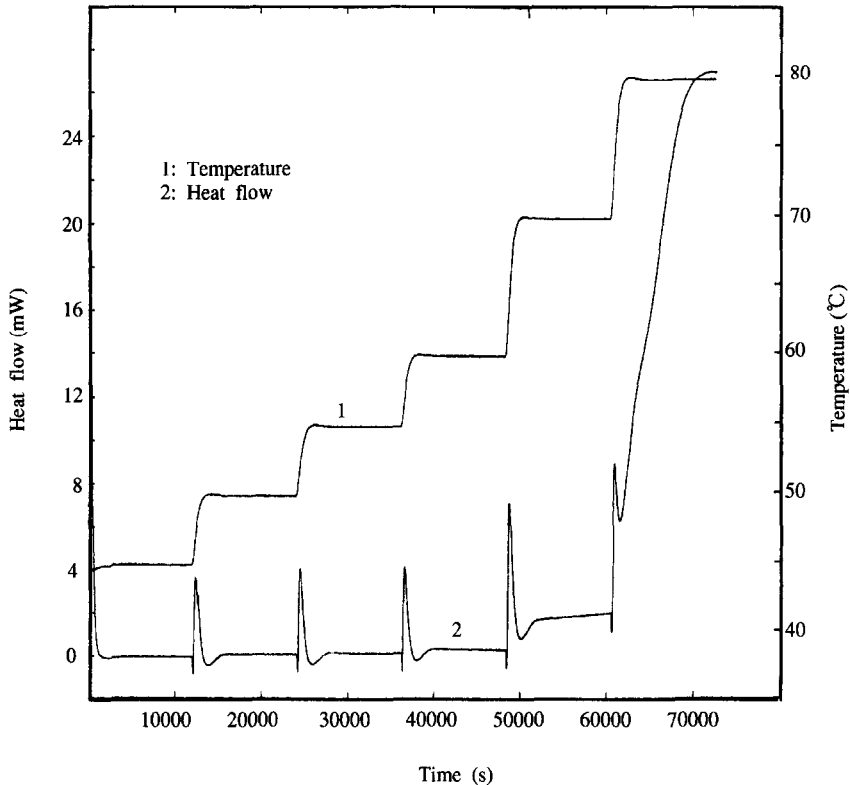


Fig. 2. Reaction heat flow at each temperature step versus time for BPB.

for the 25 kg package and the 0.51 Dewar vessel respectively, by substituting the above values for the kinetic parameters  $E$ ,  $\Delta HA$  and  $n$  and the heat transfer parameters  $S$  and  $U$  into Eq. (9).

### 3.3. Samples

The samples used in this study are listed in Table 1.

## 4. Results and discussion

### 4.1. Results

Table 2 shows the test conditions of the C80D, the results of the kinetic parameters calculated by the method mentioned in Section 2.1, and the calculated SADTs and the calculated temperatures of no return for both the 25 kg package and the 0.51 Dewar vessel.

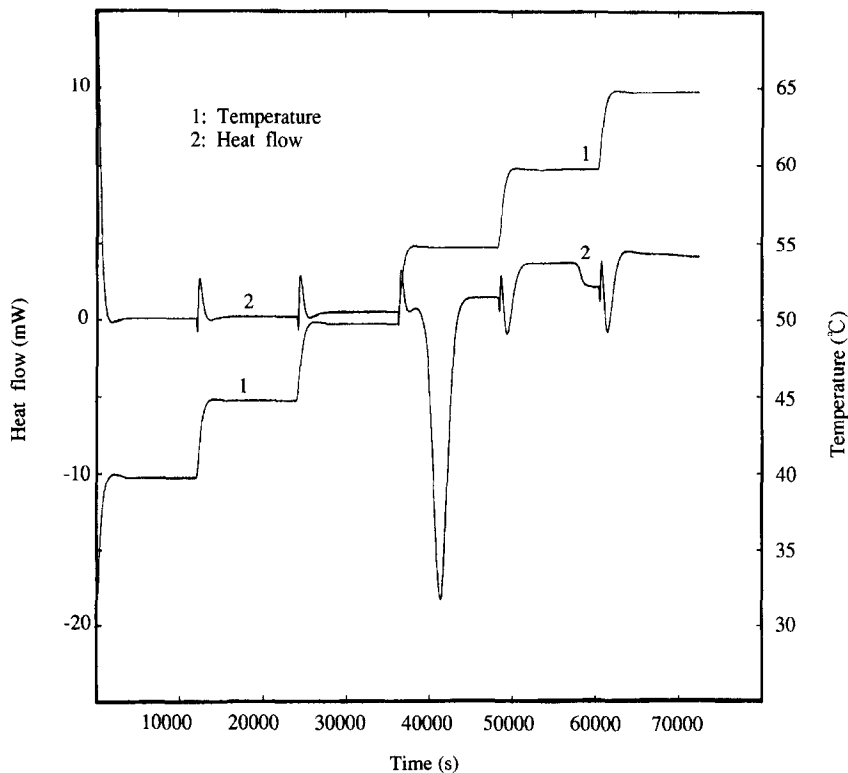


Fig. 3. Reaction heat flow at each temperature step versus time for AIBN.

#### 4.2. Comparison of calculated SADTs with US test results

The United States SADT test method [2] estimates safe storage and transportation temperatures for an organic peroxide in a specific package. The material of a 25 kg commercial package is tested in an oven held at constant temperature in order to determine the maximum temperature at which the sample undergoes auto-accelerative decomposition, provided that the temperature difference between air and the sample is not greater than 6 °C for 7 days. The temperature difference of 6 °C may be small enough for the temperature distribution in the sample to be regarded as flat, i.e., the SADT conforms to the Semenov model in the US test.

Fig. 6 shows a comparison of the calculated SADT for the 25 kg package in this study with the measured values of the US test by Fisher and Goetz [4]. Four chemicals are compared. Among three of them, BPB, CHP and AIBN, the calculated values agree well with the measured ones to within 1 °C. In the case of BPD, however, the calculated SADT is 10 °C lower than the measured one. Fig. 1 suggests that the chemical reaction mechanism at temperatures higher than 80 °C is different from that at lower temperatures, because heat flow at both 80 °C and 90 °C behaves irregularly in comparison with heat flow at temperatures lower than 70 °C. This may

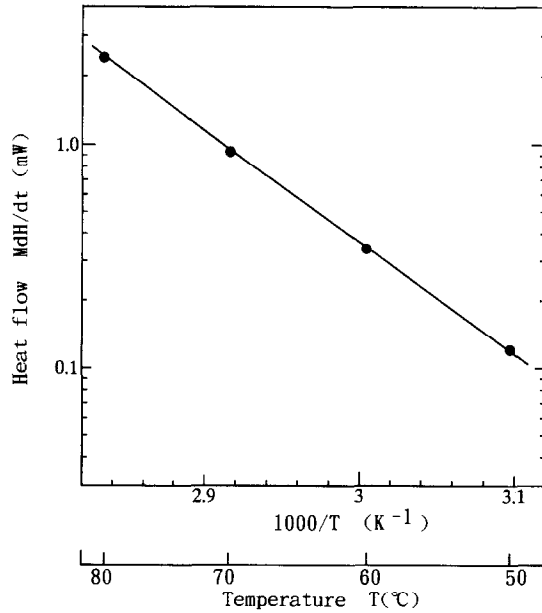


Fig. 4. Relationship between logarithmic heat flow and inverse temperature for CHP 11.2671 g.

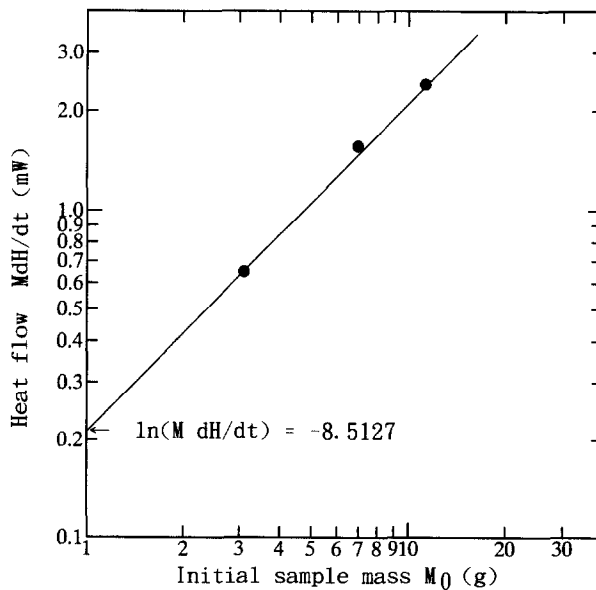


Fig. 5. Relationship between logarithmic heat flow and logarithmic sample mass for CHP at 80 °C



Table 1  
Samples of self-reactive substances

Symbols	Chemical names	Purity (%)	Solvents <sup>d</sup>	State
BPB <sup>a</sup>	<i>t</i> -butyl peroxybenzoate	99.9	(1)b	Liquid
CHP <sup>a</sup>	Cumene hydroperoxide	83.0	(1)b	Liquid
BPD <sup>a</sup>	Di- <i>t</i> -butyl peroxide	99.0	(1)b	Liquid
PMHP <sup>a</sup>	<i>p</i> -mentane hydroperoxide	53.0	(2)c	Liquid
AAP <sup>a</sup>	Acetyl acetone peroxide	34.0	—	Liquid
DIBH <sup>a</sup>	Di-isopropylbenzene hydroperoxide	54.0	(3)b	Liquid
PKHI <sup>a</sup>	Pa-kyua-HI (trade name)	—	—	Liquid
TBPA <sup>a</sup>	<i>t</i> -butyl peroxy acetate	49.9	(1)b	Liquid
BTC40 <sup>a</sup>	1,1-bis( <i>t</i> -butylperoxy) 3,3,5-trimethyl cyclohexane	39.8	(1)a	Solid
BPIB <sup>a</sup>	$\alpha,\alpha'$ -bis( <i>t</i> -butylperoxy- <i>m</i> -isopropyl)benzene	99.0	(1)b	Solid
BPO75 <sup>b</sup>	Benzoyl peroxide	75.0	(4)d	Solid
AIBN <sup>c</sup>	Azobisisobutyronitrile	99.0	—	Solid

<sup>a</sup> Produced by Nippon Oil and Fats Co. Ltd.

<sup>b</sup> Produced by Nakaraitesuku Co. Ltd.

<sup>c</sup> Produced by Kanto Chemical Co. Ltd.

<sup>d</sup> (1) Benzene, (2) toluene, (3) ethyl acetate, (4) water; a – 0.05 mol l<sup>-1</sup>, b – 0.10 mol l<sup>-1</sup>, c – 0.20 mol l<sup>-1</sup>, d – 25%.

account for the error in the calculated SADT for BPD. On the other hand, the value for BPD calculated by Fisher and Goetz [4] is relatively well coincident with the measured one. This may be because BPD was used as the standard calibration material.

#### 4.3. Comparison with SADTs by ARC

The SADTs derived using the ARC data by Fisher and Goetz [4] are also shown in Fig. 6 as a comparison with the SADTs in this study. The SADTs obtained by ARC vary more at higher and lower temperatures than the measured ones. As lower temperature ranges must be extrapolated from ARC data obtained at higher temperatures, this deviation may be attributed to the extrapolation and/or change in physical chemistry that appears in the SADT-deriving process. This theory is supported in Figs. 2 and 3. Fig. 2 shows that the heat flow of BPB at 80 °C is much higher than that predicted from heat flows at lower temperatures, resulting from a change in the chemical reaction mechanism. Fig. 3 shows the heat flow of AIBN at 55 °C, indicating incontestably the heat absorption due to phase transition.

#### 4.4. Comparison of calculated SADTs with Dewar test results

The Dewar vessel test method is standardized as a heat accumulation storage test in the UN Orange Book [2]. In the test, a cylindrical 0.5 l Dewar vessel filled with

Table 2  
Test conditions, calculated kinetic parameters and SADTs

Symbols of materials	Test conditions		Kinetic parameters			For 25 kg package		For 0.5 l Dewar vessel	
	Temperature ranges (°C)	Mass ranges $M_0$ (g)	$E/R$ ( $10^4$ K)	$\ln(\Delta H A)$ ( $\ln(Wg^{-n})$ )	Reaction order $n$	$T_{SADT}$ (°C)	$T_{NR}$ (°C)	$T_{SADT}$ (°C)	$T_{NR}$ (°C)
BPB	50–70	5.5–10.7	1.817	45.04	1.10	57	63	64	70
CHP	50–80	3.1–11.3	1.137	23.70	1.02	79	90	88	100
BPD	50–80	2.4–8.5	1.659	38.74	0.95	80	86	84	92
PMHP	60–85	10.0	1.181	26.25	1.0	67	77	74	85
AAP	50–75	8.2	1.283	30.46	1.0	55	64	61	70
DIBH	60–110	2.8–9.7	1.151	24.76	1.08	65	75	76	87
PKHI	45–65	10.4	1.624	40.48	1.0	56	63	61	68
TBPA	60–85	9.1	1.683	40.93	1.0	65	72	70	77
BTC40	60–75	1.8–6.6	2.279	58.67	1.26	50	55	58	63
BPIB	70–85	6.5	1.920	45.51	1.0	80	86	84	91
BPO75	50–80	2.0	1.249	26.84	1.0	80	90	88	99
AIBN	40–55	5.1–7.2	1.803	46.59	1.03	49	55	54	60

a 0.4 l test sample is left for at least 7 days in a test chamber held at a constant temperature. A criterion of the SADT was modified from one included in the UN Orange Book to the lowest air temperature at which an explosion or an ignition due to a self-accelerating decomposition occurs visibly or perceivably. Then, Dewar vessel tests were performed on a variety of organic peroxides, by Nippon Oil and Fats Co. Ltd. [10].

Fig. 7 shows a comparison of the calculated SADTs for the 400 ml sample held in a vessel in this study with SADTs measured by the Dewar vessel test [10]. The calculated SADTs are 1–6 °C lower than the measured ones. This discrepancy may be explained as follows. There are some differences between the assumptions involved in the Semenov model and the criterion of the Dewar vessel test. When the measured SADT is determined by recognizing the occurrence of explosion or ignition, the temperature distribution may exist on the inside of the sample. This is in conflict with the assumptions of the Semenov model. However, as Table 2 shows, differences of 5–12 °C between the SADTs ( $T_{SADT}$ ) and the temperatures of no return ( $T_{NR}$ ) are not so big that the Semenov model could be approximately applicable to a case of the SADT of the Dewar vessel test inductively.

#### 4.5. Testing assumptions for the derivation of chemical kinetic parameters

In the derivation of chemical kinetic parameters, it was assumed that the consumption of sample mass could be disregarded during an isothermal calorimetry test. In actual fact, the isothermal test was carried out for a period of 1000–1300 min at four or six temperature steps. In order to check whether or not the assumption is correct, it is necessary to estimate the consumption of sample for the duration of

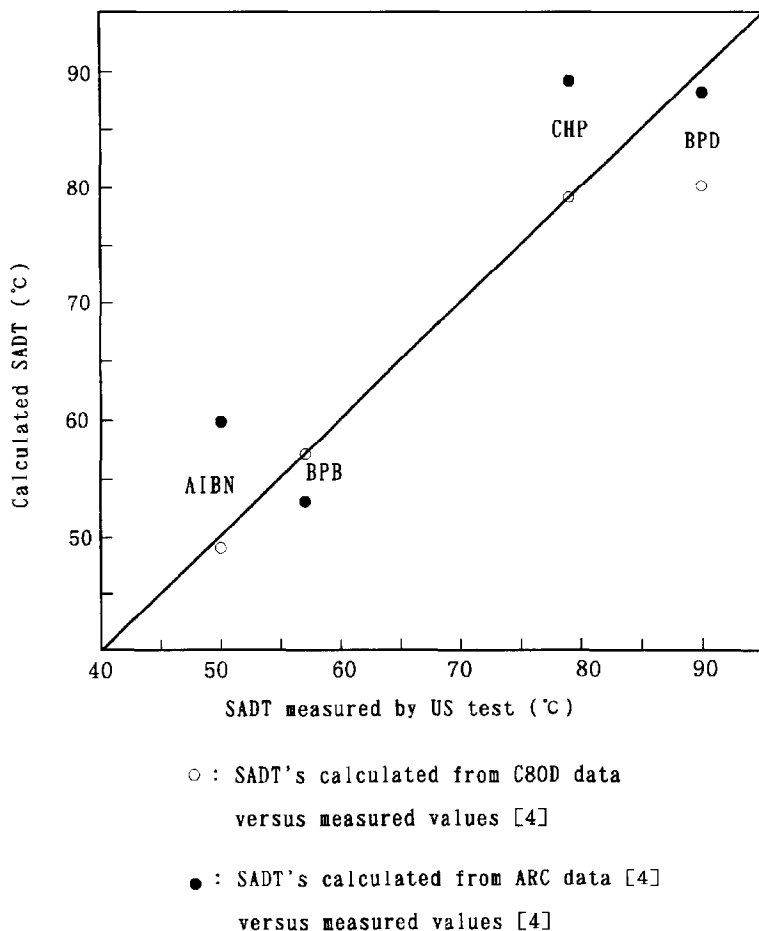


Fig. 6. Comparison between SADTs measured by US test and calculated values.

the test. For example, in the case of the BPB sample, testing was carried out up to a temperature of 70 °C for a period of 60 000 s, during which the reaction consumed only about 0.26% of the sample, calculated by dividing the total heat of about 3.38 J g<sup>-1</sup> generated for the period by the heat of the complete reaction 1318 J g<sup>-1</sup> [11]. Therefore, we can disregard the consumption of sample during the test, i.e. the assumption is seen to be correct.

## 5. Conclusions

We proposed a method to determine the self-accelerating decomposition temperature (SADT) for self-reactive substances in packaging, wherein the chemical kinetic parameters are derived from the data obtained by an isothermal heat flux reaction

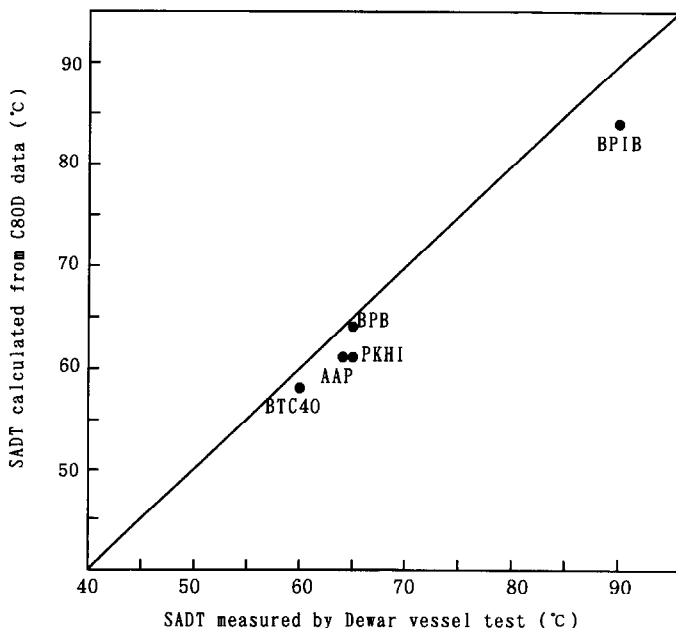


Fig. 7. Comparison between SADTs measured by Dewar vessel test and calculated values.

calorimeter (C80D) after which the SADT is evaluated from theoretical equations based on the Semenov model. The C80D, having a high sensitivity of  $10 \mu\text{W}$ , can detect heat flow due to weak reactions in the SADT temperature range. This method avoids the shortcomings of the US SADT test and the Dewar vessel heat accumulation storage test such as inefficiency, danger, complexity and so on. The evaluated SADTs coincide well with the US SADT test results and have an excellent correlation with the Dewar vessel test results. The proposed method gives more accurate results than the SADT-estimating method using data obtained by an accelerating rate calorimeter (ARC), wherein extrapolation from the data at higher temperatures to temperatures around the SADT gives rise to error. The method we have proposed could be substituted for the US SADT test method and the Dewar vessel test method.

## 6. Nomenclature

$A$	frequency factor ( $\text{g}^{1-n} \text{s}^{-1}$ )
$C_p$	specific heat per unit mass ( $\text{J K}^{-1} \text{g}^{-1}$ )
$E$	activation energy ( $\text{J mol}^{-1}$ )
$\Delta H$	heat of reaction ( $\text{J g}^{-1}$ )
$M(dH/dt)$	heat flow measured by a calorimeter ( $\text{J s}^{-1}$ )
$M$	mass of reactant (g)
$M_0$	initial mass of reactant (g)

$n$	order of reaction
$R$	gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$S$	contact area of system with surroundings ( $\text{cm}^2$ )
$t$	time (s)
$T$	temperature of system ( $^{\circ}\text{C}$ )
$T_{\text{DSC}}$	onset temperature of heat generation in a differential scanning calorimeter ( $^{\circ}\text{C}$ )
$T_0$	temperature of surroundings ( $^{\circ}\text{C}$ )
$T_{\text{NR}}$	temperature of no return ( $^{\circ}\text{C}$ )
$T_{\text{SADT}}$	self-accelerating decomposition temperature ( $^{\circ}\text{C}$ )
$U$	overall heat transfer coefficient ( $\text{J cm}^{-2} \text{K}^{-1} \text{s}^{-1}$ )

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