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Prediction and evaluation of the reactivity of self-reactive substances using microcalorimetries

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Abstract

To evaluate the thermal hazard of self-reactive substances in chemical processes, the time to maximum rate (TMR) of autocatalytic decomposition reaction of cumenehydroperoxide (CHP) was determined by calculations based on the results of isothermal measurement using DSC and heat conduction calorimeter. In addition, the factors affecting the calculated results were investigated. It was found that the TMR is affected by the catalytic action of the sample vessel metal. When this effect is taken into account in analyzing the experimental result, the predicted TMR shows a good agreement with the value determined using the adiabatic reaction calorimeter. The present study clarified that the proposed technique would enable the appropriate evaluation of thermal hazard of an autocatalytic reaction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Self-reactive substance; CHP; Autocatalytic reaction; TMR; Microcalorimetry

1. Introduction

In recent years various kinds of substances have been used in the chemical industry and the demand of appropriate evaluation method of the thermal hazards of reactive chemicals is increasing. They are often operated in the potentially dangerous situation. For the safety/risk assessment of the chemical process, the prediction and evaluation technique considering the process and environmental conditions are strongly required [1–3].

Since a chemical process system consists of unit operations for reaction, refining and storage etc., evaluation based on the characteristics of each process enables the thermal hazards associated with a chemical substance to be evaluated. The storage, drying or distillation process, during which a substance is exposed to a constant temperature for an extended time, may cause a decomposition of the chemical substance, and the decomposition reaction may result in a runaway reaction. The quantitative relation between the temperature and the time of the substance entering into a runaway reaction is essential to prevent a runaway reaction and an accidental explosion.

From a point of view of reaction mechanism the decomposition reaction can be classified as either a general *n*th order reaction or an autocatalytic reaction. The former reaction allows the temperature–time relationship to be forecast using the kinetics of reaction, and the latter reaction has a complicated reaction

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mechanism and is not easy to handle quantitatively [4,5]. Since an autocatalytic reaction generates a product that is composed of catalytic ingredients, the catalytic ingredients increase as the reaction progresses, and the reaction progresses in an accelerating manner. Therefore, it is difficult to predict the temperature rise that is associated with this type of reaction.

In general the thermal hazard of a chemical substance is evaluated by measuring the onset temperature, the heat of reaction and/or the self-accelerating decomposition temperature (SADT) [6–9]. However the time required to reach the maximum self-heating rate, usually called as the time to maximum rate (TMR), is more suitable parameter for the safety evaluation of a chemical process in which reactive chemicals are used [4–6]. Because TMR indicates the time available for taking defensive or mitigation measures in process upset situations. Although TMR is usually determined with sensitive calorimeters under an adiabatic condition, these devices are expensive and their operation requires a lot of time and skill [10,11].

The present paper describes a technique for determining TMR by measuring the self-heating behavior of a self-reactive substance, cumenehydroperoxide (CHP), during isothermal measurement using a conventional differential scanning calorimeter (DSC) and a heat conduction calorimeter (Setaram C80). In addition, factors that affect the calculation of the TMR of CHP are discussed to evaluate the thermal hazard associated with CHP. Finally the TMRs determined by DSC and C80 calorimeter were compared with TMR determined by an adiabatic calorimeter ARC.

2. Experimental

2.1. Experimental apparatus and methods

A DSC (Shimadzu DSC-50), a heat conduction calorimeter (Setaram C80), and an adiabatic calorimeter (Columbia Scientific, accelerating rate calorimeter: ARC) were used in the present experiment. A sealed cell made of SUS-304 stainless steel was used in the DSC, and a pressure vessel made of SUS-316 stainless steel was used in the C80. In the experiment, nitrogen gas was purged in the cell and the vessel. An empty vessel was used as a reference. The sample mass was approximately 2 mg for DSC measurement and 1–3 g for C80. For ARC measurement, a sample bomb made of hastelloy C was used and the sample mass was approximately 0.9 g. ARC, DSC and C80 measurements were performed according to the following procedures:

- ARC
  The sample was heated at the rate of 3 K min^{-1} to a predefined set temperature and was maintained adiabatically until the exotherm was detected. The sample was maintained under an adiabatic condition even after the exotherm was detected and TMR was measured at several predefined temperatures.
- DSC and C80
  Heating scanning: The sample was heated from room temperature to 573 K (523 K for C80) at the rate of 10 K min^{-1} (2 K min^{-1} for C80) in order to measure the onset temperature T_{DSC} K, T_{C80} K and the heat of reaction Q_{DSC} J g^{-1}, Q_{C80} J g^{-1} of the main reaction.
  Isothermal scanning: The temperature of the sample was raised at the rate of 20 K min^{-1} (2 K min^{-1} for C80) until reaching a predefined set temperature, and the sample was then maintained at this temperature. The induction time to exothermic reaction and the heat of reaction were measured under isothermal condition at several temperatures lower than T_{DSC} or T_{C80} which was obtained by usual heating measurement.

2.2. Material

The material used in this study was CHP (80 wt.%) with cumene solvent (20 wt.%). The thermal decomposition of CHP is regarded as autocatalytic and the catalytic ingredients are organic acids such as formic and acetic acids [12,13]. Some parameters on the thermal decomposition behaviour of CHP were published and SADT determined by several test methods were reported in the range of 352 and 362 K [9,11,14,15].

3. Prediction of adiabatic self-heating curve

TMR was calculated using the equation described by Grewer [16] for predicting temperature rise based on the assumption that adiabatic self-heating is a 0th order reaction, where the consumption of the reactant at the early stage of decomposition could be ignored. The calculation procedure is as follows:

Using Eq. (1), which holds for an isothermal condition, the isothermal results are plotted as the thermal conversion rate u on the horizontal axis and the product of self heat rate q and the density ρ on the vertical axis. Since the reaction rate constant k does not change under isothermal conditions, k was calculated from the slope of the linearity-maintained range and the autocatalytic coefficient β was calculated from the intercept. Here, the autocatalytic coefficient β characterizes the self-acceleration of the reaction and is greater than 0 but smaller than 1. The smaller the coefficient β, the greater the effect of self-acceleration. The application range of the thermal conversion rate based on the assumption that the thermal decomposition reaction is of the 0th degree is defined as ''an area where linearity in the u–q diagram can be maintained with the detection limit of the device as the lower limit''.

$$q\rho = Q(\beta + u)k = Qku + Qk\beta \quad (1)$$

where q is the heat flow rate (W kg^{-1}), ρ the density (kg m^{-3}), Q the heat of reaction (J mol^{-1}), β the autocatalytic coefficient, u the thermal conversion rate, and k the reaction rate constant (mol m^{-3} s^{-1}).

Using an Arrhenius plot, the apparent activation energy E and the pre-exponential factor A were calculated from k calculated at each isothermal holding temperature. The temperature–time curve was calculated by assigning the calculated parameters, experimentally determined values and properties into Eq. (2).

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{Q}{\rho C_p}(\beta + u)A \exp\left(\frac{E}{RT}\right) \quad (2)$$

where, T is the temperature (K), t the time (s), C_p the specific heat capacity (J kg^{-1} K^{-1}), A the pre-exponential factor (mol m^{-3} s^{-1}), F the apparent activation energy (J mol^{-1}) and R the universal gas constant (J mol^{-1} K^{-1}). In this paper TMR is defined as ''the time until the heating rate exceeds 1000 K min^{-1}''. In order to calculate TMR at each holding temperature, the heat of reaction Q, autocatalytic coefficient β and predefined set temperature T are substituted into Eq. (2) and integrated at a each time step Δt to calculate the temperature rise. Considering the heat loss during the isothermal measurement, the value obtained by heating scanning was adopted for the heat of reaction Q.

For TMR calculation, the autocatalytic coefficient β at each temperature was used. From the ln TMR vs T^{-1} plot TMR was obtained by extrapolating from the approximate linear line into the lower temperature region.

4. Results and discussion

4.1. ARC measurement

According to the results of DSC measurement, the onset temperature T_{DSC} was obtained as 440 K. For ARC measurement, the predefined holding temperature until the start of adiabatic temperature rise was set to 364, 370, 374, 379 and 383 K. The pseudo-adiabatic condition was maintained during ARC measurement. However, since the heat liberated by the decomposition of the sample is also consumed by the sample bomb, the data must be corrected for the thermal inertia of the system using Eq. (3). The thermal inertia is well known as a phi factor (Φ) and if the sample vessel absorbs no heat (i.e., the system is completely adiabatic), then Φ=1 [10].

$$\Phi = 1 + \frac{(m(\mathrm{bomb}) \times C_p(\mathrm{bomb}))}{(m(\mathrm{sample}) \times C_p(\mathrm{sample}))} \quad (3)$$

where Φ is the thermal inertia factor, m(bomb) the mass of the bomb (g), C_p(bomb) the specific heat capacity of the bomb (J kg^{-1} K^{-1}), m(sample) the mass of sample (g), and C_p (sample) the specific heat capacity of the sample (J kg^{-1} K^{-1}). Since TMR. is affected by the thermal inertia factor as well as the temperature rise and the heat of reaction measured by the experiments, TMR data should be corrected using Eq. (4) [11,17].

$$\tau = \frac{\tau_{\mathrm{obs.}}}{\Phi} \quad (4)$$

where τ is the corrected TMR (min) and $\tau_{\mathrm{obs.}}$ is the experimentally observed TMR (min).

Since the mass of the sample was measured to be approximately 0.9 g, the value of Φ is approximately 5.0. However it was already found that the influence of

Table 1
Observed and corrected TMRs of CHP determined by ARC experiments

Holding temperature (K)	τ_{obs}. (min)[a]	τ (min)[b]
364	2750	550
370	1510	300
374	833	167
379	563	113
383	454	91

[a] Experimentally observed TMR.
[b] Φ-corrected TMR.

the mass of the sample had a negligible in the ARC experiment for CHP and almost the equal TMR was obtained [18]. Table 1 lists the experimentally observed and corrected values of TMR based on the ARC measurement. After the thermal inertia correction, using the corrected 5 point data, the relationship between TMR and predefined holding temperature is obtained as follows:

$$\ln \tau = -29.7 + 1.31 \times 10^4 \left(\frac{1}{\mathrm{T}}\right) \quad (5)$$

From this equation TMR at each holding temperature can be calculated and it would be an useful information for the process control and safety evaluation.

4.2. Isothermal DSC measurement

According to the results of DSC measurement, the onset temperature and the heat of reaction were obtained as 440 K and 1140 J g^{-1}, respectively. For isothermal measurement, the predefined holding temperature was set from 383 to 403 K in 10 increments according to the onset temperature and measurement time. Table 2 lists the heat of reaction obtained by isothermal DSC measurement $Q_{DSC-ISO}$ and Fig. 1 shows the temperature–time curves at each holding temperature.

Table 2
Heats of reaction of CHP determined by heating and isothermal DSC

Scanning	Heat of reaction $Q_{DSC-ISO}$ (kJ g^{-1})
Heating	
10 K min^{-1}	1.01
Isothermal	
383 K	0.76
393 K	0.57
403 K	0.61

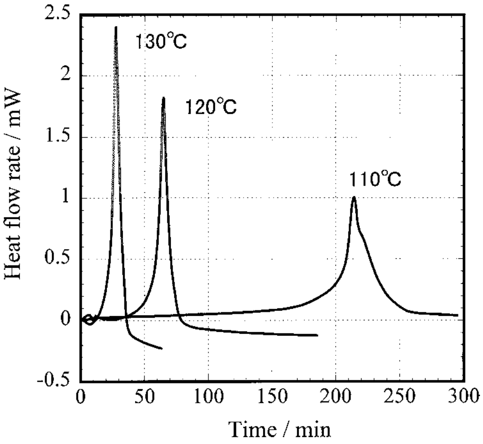

Fig. 1. Isothermal DSC curves of CHP.

As Table 2 shows, $Q_{DSC-ISO}$ were from 50 to 67% of Q_{DSC}. This is because determination of the exothermic peak area at isothermal measurement is difficult. And also the decomposition gradually proceeded during the isothermal induction period and the small heat of reaction below the detection level of DSC was liberated and then the sample might have been consumed before the main reaction.

Based on the isothermal measurement results, the temperature–time curve under an adiabatic condition was drawn and TMR was calculated by the previously mentioned procedure. Fig. 2 shows the comparison of the calculated TMR based on the isothermal DSC measurement results and that based on the adiabatic ARC results. TMR based on the isothermal DSC results and the holding temperature have the following relationship:

$$\ln \tau = -25.8 + 1.07 \times 10^4 \left(\frac{1}{\mathrm{T}}\right) \quad (6)$$

In Fig. 2, the TMR calculation result obtained by isothermal DSC is shorter than that obtained by ARC measurement. This means that either accelerating factor other than the autocatalytic ingredients affect the reaction or that the reaction mechanism is different between the ARC and the DSC measurements. The difference in experimental conditions between ARC

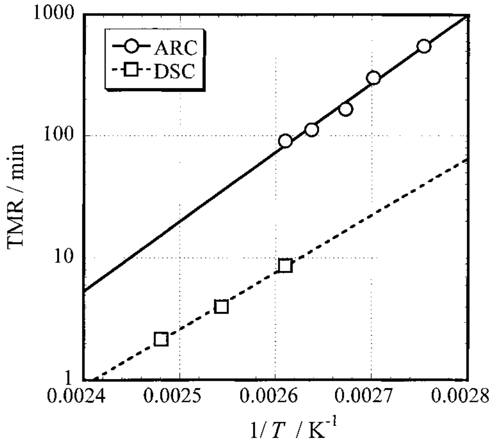

Fig. 2. Comparison of calculated TMR by isothermal DSC and ARC.

and DSC measurements is considered to be as follows: For ARC measurement, sample of several gram order is loaded in a spherical sample bomb made of hastelloy C. For DSC measurement, sample of several milligram order is loaded in a cylindrical cell made of SUS-304 stainless steel. Therefore, the cell has a large spatial volume ratio and the bottom of the cell is covered with the sample like a thin film in the DSC measurement. Since the sample has a wide contact area with the gas phase in DSC cell, catalytic ingredients of reaction products may be emitted into the gas phase to promote the reaction. And another possibility is that the catalytic action may occur because the containers are constructed of different metals.

As the sample mass is small in DSC measurement, a slight heat liberated during isothermal measurement and the catalytic action of the cell metal may affect the results. Therefore, the results of calculation based on DSC measurement may not give a proper indication of the thermal hazard. These factors including the ratio of sample mass to the contact areas should be studied for the varied sample masses. C80 calorimeter was used for the next step because this method allows a comparatively greater sample mass to be used.

4.3. Isothermal C80 measurement

If the sample vessel has a large capacity and the mass of the chemical substance in the vessel is large, the emission of catalytic ingredients from the liquid phase to the gas phase and the effect of a catalytic action associated with the vessel wall will be reduced. Then the progress of the reaction becomes significant, not in the gas phase but in the liquid phase. The effects of the catalytic action of a stainless steel vessel and the sample mass on TMR calculation results were investigated.

4.3.1. Effect of the catalytic action of a stainless steel vessel

In order to discuss the catalytic action of the stainless steel vessel, the effect of the contact between the sample and the sample vessel on the TMR calculation was investigated by using the inner glass vessel.

Sample was placed in a sample vessel with an inner glass vessel to prevent the sample from being contact with the sample vessel, and sample was also placed directly into a sample vessel. The sample was measured isothermally for both vessels. The sample mass was 2.0 g in both vessels. Table 3 lists the heat of reaction obtained by isothermal measurement and Figs. 3 and 4 show the measurement results of various holding temperatures in each vessel.

Table 3 indicates that the inner glass vessel did not change $Q_{\mathrm{C80\text{-}ISO}}$ significantly. While Figs. 3 and 4 indicate that the maximum heat flow rate without the inner glass vessel is approximately twice of that using the inner glass vessel. The temperature–time curves

Table 3
Heats of reaction of CHP determined by C80 calorimeter with and without inner glass vessel

Holding temperature (K)	$Q_{\mathrm{C80\text{-}ISO}}$ without glass vessel (kJ g^{-1})	$Q_{\mathrm{C80\text{-}ISO}}$ with glass vessel (kJ g^{-1})		
	Sample mass 2.0 g	1.0 g	2.0 g	3.0 g
383	0.76	0.76	0.84	0.84
388	0.97	0.86	0.86	0.90
393	0.94	0.86	0.90	0.87
398	1.00	0.92	0.94	0.91

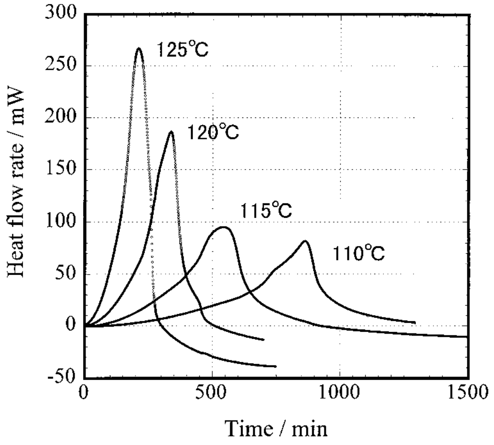

Fig. 3. Isothermal curves of CHP by C80 calorimeter without inner glass vessel.

also indicate that the reaction is accelerated before reaching the maximum heat flow rate. Comparing the results of C80 measurement with the inner glass vessel and those of DSC shown in Fig. 1, the DSC results show an even sharper profile of the heat flow rate, and the maximum heat flow rate per unit sample mass is 0.9 W g^{-1} for DSC and 0.045 W g^{-1} for C80 at the isothermal holding temperature of 393 K and the ratio is about 20:1.

Fig. 5 shows the relationship between the holding temperature and TMR according to the previously mentioned procedure. The relationship of both cases are obtained as follows:

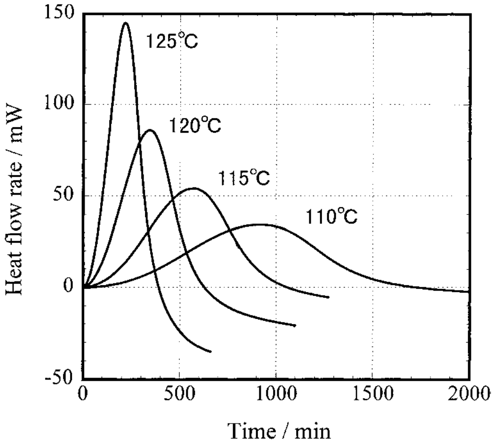

Fig. 4. Isothermal curves of CHP by C80 calorimeter with inner glass vessel (CHP 2.0 g).

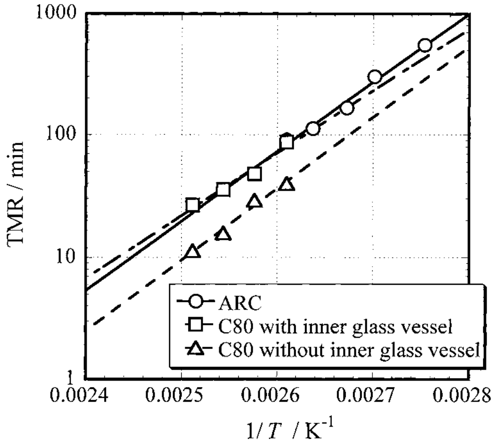

Fig. 5. Comparison of calculated TMRs by isothermal C80 and ARC.

without inner glass vessel :

$$\ln \tau = -31.3 + 1.34 \times 10^4 \left(\frac{1}{T}\right) \tag{7}$$

with inner glass vessel :

$$\ln \tau = -26.6 + 1.18 \times 10^4 \left(\frac{1}{T}\right) \tag{8}$$

There is a significant difference between with and without the inner glass vessel for the relationship of TMR and the holding temperature, and the results of measurement using the inner glass vessel shows a good agreement with the ARC results in the applied temperature range.

The above discussion indicates that contact between the sample and the sample vessel tends to reduce the TMR and when the sample does not contact the metal vessel the TMR value closely matches the ARC result. When the sample contacts the metal vessel the self heat rate becomes larger than that with a glass vessel, the sample is consumed faster and the time to complete the reaction is reduced. Therefore, it is concluded that the stainless steel vessel (SUS-316) is thought to be an accelerating factor with respect to the sample decomposition and the catalytic action by the stainless steel vessel has a large influence on the TMR. Although the use of the inner glass vessel causes a larger heat capacity and delay in heat conduction, as observed in the exothermic peak profile, the difference in reaction kinetics due to the catalytic action of the stainless vessel is thought to be more predominate than the difference in the heat transfer. Further experiments are needed for the quantitative discussion.

4.3.2. Effect of sample mass

The effect of sample mass on the TMR calculation was investigated by performing C80 measurement. Sample mass was varied according to the spatial volume in the vessel in order to discuss the possibility of decomposition progressing in the gas phase. The sample mass was set to 1.0, 2.0 or 3.0 g. Since the catalytic action of the stainless steel vessel affects the decomposition behaviour of the sample as studied in the previous section, the inner glass vessel was used to eliminate the effects of the catalytic action. According to this experimental set-up, the inner volume of the C80 vessel becomes ca. 3.8 ml and the filling ratio of sample become ca. 26, 53 and 79%, respectively. Considering the onset temperature of exothermic reaction and measurement time, the holding temperature for isothermal measurement was set from 383 to 398 K in 5 increments. Table 3 lists the heat of reaction obtained by isothermal measurement and Figs. 4, 6 and 7 show the measurement results.

In Table 3, $Q_{C80\text{–}ISO}$ are smaller than that obtained in heating scanning measurement Q_{C80} (1.14 kJ g^{-1}), and the maximum self heat rates per unit mass are similar at each sample mass and holding temperature. And, as shown in Figs. 4, 6 and 7, self heat rate profiles are similar.

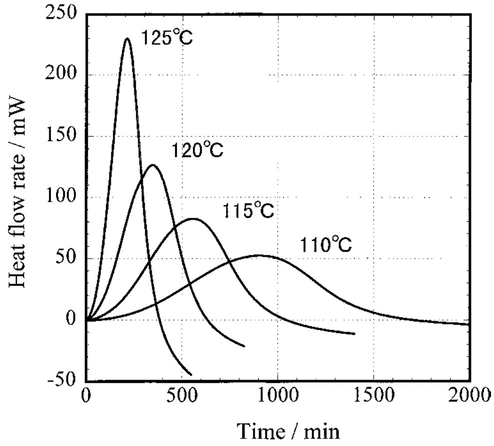

Fig. 7. Isothermal curves of CHP by C80 calorimeter (CHP 3.0 g).

Fig. 8 shows the influence of the sample mass on the calculated TMR of isothermal C80 with the ARC result. If catalytic ingredients are emitted into the gas phase, the concentrations of the catalytic ingredients in the liquid phase become lower depending on the spatial volume ratio because of the equilibrium between gas and liquid and that affect the self heating behavior and TMR values. However, the TMR obtained at each sample mass showed good agreement within the experimental error, and it indicates that the catalytic ingredients, such as formic, acetic and other organic acids, are not emitted into the gas phase. So the organic acids of the reaction product are dissolved and kept in the liquid phase and the decomposition proceed in the liquid phase. As the relationship between TMR and the holding temperature when

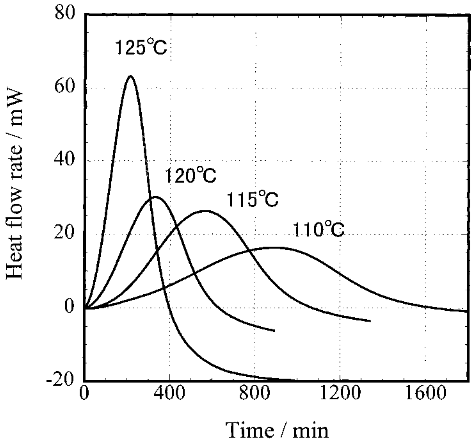

Fig. 6. Isothermal curves of CHP by C80 calorimeter (CHP 1.0 g).

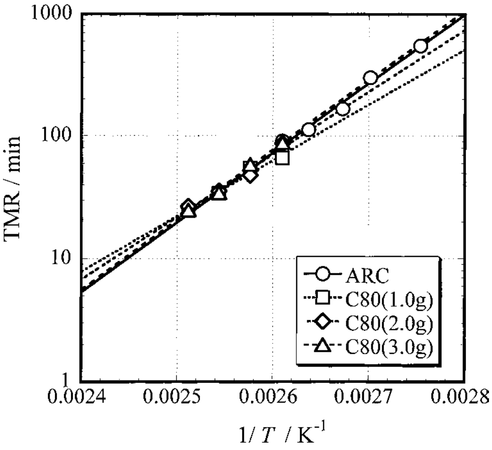

Fig. 8. Influence of sample mass of CHP on the calculated TMR.

the sample mass was 3 g in C80 was determined as the following equation and it is perfectly matched with the ARC results shown as Eq. (5).

$$\ln\tau = -29.8 + 1.31\times 10^4\left(\frac{1}{\mathrm{T}}\right) \qquad (9)$$

Therefore, the sample mass may not affect the results significantly. Moreover, since ARC is an sensitive adiabatic calorimeter with a spherical sample bomb, the vertical temperature distribution in the sample bomb of ARC is smaller (estimated as within 0.5 K [19]) than that of C80 having larger and cylindrical shape. The emission of the ingredients from liquid to gas phase is not negligible in C80 measurement, so that the larger mass of sample is preferable. When C80 calorimeter is used for the safety evaluation of self-reactive substance with autocatalytic reaction, a sample mass of 2 g or greater and the filling ratio in the vessel of 50% or more is recommended. From the above results it is concluded that the technique presented in this paper permits the quantitative evaluation of a runaway reaction of CHP showing an autocatalytic reaction. It is very useful for the safety assessment and the process optimization.

5. Conclusion

In order to evaluate the thermal hazard of self-reactive substances in a chemical process, the time to maximum rate of autocatalytic reaction of the thermal decomposition of cumenehydroperoxide was determined by calculations based on the results of isothermal measurement using DSC and a heat conduction calorimeter C80. Both the results were compared with those of an adiabatic calorimeter ARC. The results of the investigation are as follows:

1. In DSC measurement using a stainless steel cell, the hazard of an autocatalytic reaction of CHP cannot be evaluated because of the small sample mass and the catalytic action of the cell metal.
2. In C80 measurement, the catalytic reaction of the stainless steel vessel had a larger influence on the thermal decomposition of CHP than the sample mass. And less reactive material with the sample, such as glass vessel, was found to be effective for the evaluation of the reactivity of reactive chemicals.
3. Using TMR as an index, the thermal hazard of CHP was evaluated based on isothermal C80 measurement results. When the inner glass vessel was used, the C80 enables ARC equivalent evaluation using a sample mass of 2 g or greater. By taking into account the factors that affect the TMR values, the thermal hazard associated with an autocatalytic reaction can be appropriately evaluated.

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