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THERMAL DECOMPOSITION KINETIC OF REACTIVE SOLIDS BASED ON ISOTHERMAL CALORIMETRY MEASUREMENTS

X.-R. Li[*] *and H. Koseki*

National Research Institute of Fire and Disaster, 14-1, Nakahara 3-Chome, Mitaka-shi, Tokyo 181-8633, Japan

An isothermal method was applied to measure the thermal decomposition of reactive solids in a sensitive heat flux reaction calorimeter, C80. This technique experimentally clarified the decomposition mechanisms of unstable substances based on the shapes of the heat flow curves, from which autocatalysis, first-order reaction or pseudo-autocatalytic reaction could be recognized. Kinetic parameters were derived from the measured data.

Keywords: *decomposition, isothermal method, reaction mechanism, self-accelerating decomposition temperature*

Introduction

It is believed that the limitation of clarifying the mechanism of reaction interferes the determination of the accurate kinetic data [1–3]. The challenge is to find a general analytical method that allows the determination of the cause/scheme as well as the rate of reaction for a wide range of materials. Traditionally the reaction mechanism of a compound can be determined by chemical techniques, such as HPLC (high pressure liquid chromatograph) and NMR (nuclear magnetic resonance), in which the reaction process is usually dependent upon the change of the concentration of the compound occurring in solution or gas phase. However, since the reaction mechanism is normally complicated, in particular for long, slow reactions or for reactions that take place in solid state, the analytic procedure is much more complex due to the difficulty on measuring the concentration in the reaction. Hence the chemical methods are limited only to characterize some elementary reactions. Alternatively, all physical and chemical processes are accompanied with heat exchange, thus the signal from heat production in a reaction, providing an appropriate way is adopted, can in turn give information to get access to the true parameters for the reaction.

An analytical procedure was reported in this paper to characterize the reactions and the decomposition kinetics for organic peroxides or similar materials at the temperature range covering their own self-accelerating decomposition temperatures (SADTs) by means of a heat flux reaction calorimeter C80. The SADT is defined as the lowest ambient temperature at which auto-accelerative decomposition of an unstable substance occurs and is considered as a safety margin of the materials. Hence the thermal character of these substances near the SADT should be firstly clarified. Several solids were concerned.

Principle

Organic peroxides or self-reactive materials are types of self-reactive compounds. If the reaction is basically accelerated by temperature increment and thus the rate of reaction depends only upon the temperature, it follows an *N*-order rate law, that is, the one way reaction which goes from the reactant A to the product B; Whereas if at the initial stage some amount of the product B is generated and then it may inversely trigger self-acceleration, the scheme of the reaction represents the model of autocatalysis. The principles of the reactions and corresponding kinetic equations are described as the following two formulas [3–5]:

$$\mathrm{A}\rightarrow\mathrm{B}\quad \mathrm{d}\alpha_t/\mathrm{d}t=k(1-\alpha_t)^{\mathrm{N}}\quad N\text{-order reaction} \tag{1}$$

$$\begin{cases} A\rightarrow B \\ A+B\rightarrow 2B\quad \mathrm{d}\alpha_t/\mathrm{d}t=k\alpha_t^{1-x}(1-\alpha_t)^{1-y}\ \text{autocatalytic} \end{cases} \tag{2}$$

where α_t is the fraction of the reaction which has occurred at a certain time, $\mathrm{d}\alpha_t/\mathrm{d}t$ is the rate of reaction, N, $(1-x)$ and $(1-y)$ are the fitting constants characteristic of the reaction rate law. Besides the above two schemes, for solids there is the third likelihood of the reaction that if the reaction is accompanied by the phase transformation like melting in the compound, the reaction will behave as namely pseudo- autocatalysis or pseudo-*N*-order reaction. Examples of standard reaction curves characteristic of different reaction rate laws were given by Ng [5] and Hansen [6].

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[*] Author for correspondence: li@fri.go.jp

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

After the measurement of reaction curves, the rate law of reaction could be judged by comparing their shapes with those of model curves. In Eqs (1) and (2), k is a general form of the rate constant for the reaction, and is controlled by the Arrhenius law.

$$k = A\exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor, R the gas constant, T the absolute temperature, and E the activation energy of the reaction and a characteristic parameter that defines the temperature dependency of a reaction.

In this paper activation energies and other kinetic parameters were determined by an isothermal calorimetry. The thermal calorimeter monitors the rate of a process in term of heat flow (J s^{-1} or Watts, W). The relation between the rate of heat production and the rate of reaction is obtained by normalizing heat flow data with respect to the amount of sample:

$$\begin{aligned} q_{\mathrm{t}} &= \mathrm{d}Q_{\mathrm{t}}/\mathrm{d}t = -\Delta H D_0 \mathrm{d}\alpha_{\mathrm{t}}/\mathrm{d}t = \\ &-\Delta H D_0 k \alpha_{\mathrm{t}}^{1-x}(1-\alpha_{\mathrm{t}})^{1-y} \end{aligned} \tag{4}$$

($\mathrm{d}Q_{\mathrm{t}}/\mathrm{d}t$) or q_{t} is the heat flow at time t, D_0 the amount of sample, k the rate constant, and ΔH the reaction enthalpy. Thus, if the heat flow at certain time and the reaction enthalpy are known, the rate constant can be calculated. α_{t} is obtained by the ratio of integration of the heat flow over a certain time during the reaction to that within the whole reaction. Since α_{t} is a function of time, heat flow must be a function of time too. This function plotted as the reaction curve was also measured by the calorimetry. The rate laws of different samples were ascertained from the shapes of the heat flow curves, and the activation energies of the reactions were determined from the Arrhenius plots.

Experimental

As listed in Table 1, three solid samples, benzoyl peroxide (BPO), lauroyl peroxide (LPO) and 1,1'-azobis(cyclohexane-1-carbonitrile) (ABCN), were selected for analysis. The sample under test was placed in a 12 mL stainless steel vessel, which was loaded into the central channel. The heat flow from a reaction studied diffused from the reaction site to the heat sink or vice versa. The thermopiles used were extremely sensitive and were capable of measuring a reaction with a heat flow of several μW. All the temperatures in the tests were chosen as close to the referenced SADT values, which are 75°C for BPO, 49°C for LPO and 82°C for ABCN [7, 8], respectively in a 500 mL Dewar vessel.

C80 is a heat flux calorimeter manufactured by SETARAM of France, having the reputation of high sensitivity. Isothermal experiments were conducted in this research. The calorimeter is equipped with two ampoule channels. Both channels were placed in a big block sink that was finely controlled at the set temperature by a series of thermostats. The instrument was connected to a computer in order to facilitate data collection, evaluation and curve plotting.

Meanwhile, for the purpose of comparison, non-isothermal tests were also carried out for each sample of 0.5 g at a scanning rate of 0.1 K min^{-1}, which detected the heat flow and pressure from the room temperature to 200°C. The measurements were performed in both stainless steel (SUS) and glass vessels in order to check whether there is redox effect from the vessel materials on the samples as concerned in this paper.

Results and discussion

Characteristics of decomposition and kinetic parameters of BPO

The reaction curves of heat flow *vs*. time of BPO at 65, 70, 72, 74, 75 and 80°C were shown in Fig.1 and the curves of heat flow and pressure *vs*. temperature in a scanning test of BPO at 0.1 K min^{-1} were drawn in Fig. 2. Both figures showed that the reactions of BPO occurred in solid state, since no endothermic effect appearred during the whole reaction in either isothermal or non-isothermal measurement. The non-isothermal measurement showed that there was no catalytic effect on the reaction of BPO from the materials of the vessels. And an intense reaction of BPO occurred at an onset temperature about 95°C. In con-

Table 1 Samples used in the tests

Code	BPO	LPO	ABCN
Sample name	Benzoyl peroxide	Lauroyl peroxide	1,1'-azobis(cyclohexhane-1-carbonitrile)
State	solid	solid	solid
Purity	74.5% with water	99.3	99.0
Amount/g	0.50±0.01	0.50±0.01	0.50±0.01
Temperature/°C	65, 70, 72, 74, 75, 80	48, 50, 53, 55, 57, 60	83, 85, 87, 90

Samples were from Aldrich Co. Ltd.

trast in the isothermal measurement, the reaction of BPO started at much lower temperatures (from 70°C), which was at the range of its SADT (75°C). The isothermal measurement also provided the information on the pattern of the reaction. In Fig. 1, each reaction curve initially went up, and after reaching a maximum it went down. The shape of the reaction curves is characteristic of an autocatalytic reaction at all temperatures studied. The reason can be explained as follows. At each constant temperature, an intermediate free radical (as product *B* in Eq. (2)) [3] was generated and thus it caused the rate of reaction, as well as heat flow, to increase gradually until reaching the climax. During this stage the intermediate free radical behaved as product, whose concentration was rising in value, though its generation and consumption were simultaneously happening all the time. After the climax was reached the consumption of the intermediate product tended to be dominant and the heat flow decreased with the time. So the conversion ratio of the intermediate product *B* controlled the rate of reaction.

There are four parameters in Eq. (2) that determine the observed signals for autocatalytic reaction of BPO: *A*, *E*, (1–*x*), and (1–*y*). With the testing temperature decreases, the value of the climax of the curves reduces and the time taken to this point becomes longer. Each maximum point consists of two parameters: the ordinate q_m and the abscissa t_m. For the purpose of evaluating the activation energy, only the rate of heat evolution at the maxima is needed, since it should typically follow the Arrhenius law with temperature. But it is thought that t_m has the similar temperature dependence. The activation energy can be obtained from the variation of q_m with temperature.

$$(q_m/D_0)=-\Delta Hk\alpha_m^{1-x}(1-\alpha_m)^{1-y}= A''k=A'''\exp(-E/RT) \quad (5)$$

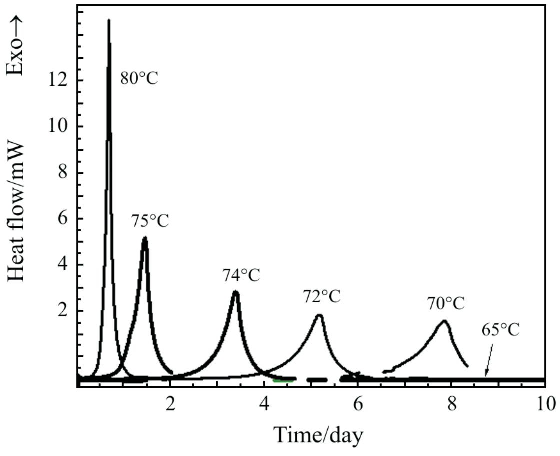

Fig. 1 Isothermal reaction curves of BPO

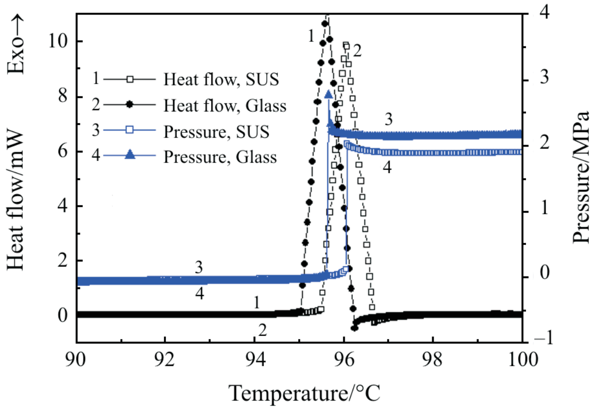

Fig. 2 Non-isothermal reaction curves of BPO (heating rate: 0.1 K min^{-1})

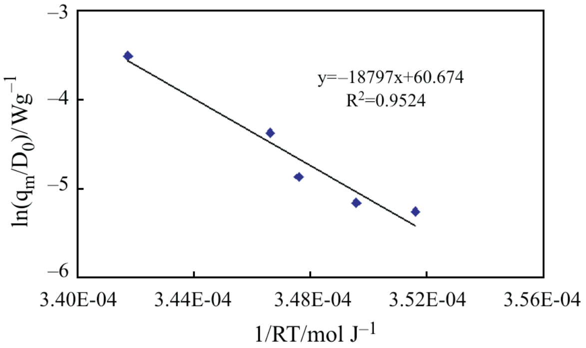

Fig. 3 Determination of activation energy from the slope of $\ln(q_m/D_0)$ *vs.* $1/RT$

where α_m is the value of α when the rate of the reaction is at the maximum. The linear regression of the logarithmic form of q_m/D_0 data, $\ln(q_m/D_0)$ *vs.* $1/RT$ according to Eq. (5) yields a straight line in Fig. 3 and the slope is proportional to the activation energy as shown in Table 2.

Furthermore, Eq. (4) is expressed in logarithmic form

$$\ln(q_t/D_0)=\ln(-\Delta Hk)+(1-y)[\alpha\ln\alpha_t+\ln(1-\alpha_t)] \quad (6)$$

in which *a* is a constant defined as the ratio of (1–*x*) to (1–*y*). At the point of maximum heat flow in Fig. 1, the differential of $d\alpha_t/dt$ at each temperature is zero. From $d(d\alpha_t/dt)|_{max}=0$, *a* can be obtained for autocatalytic reaction from:

$$a=(1-x)/(1-y)=\alpha_m/(1-\alpha_m) \quad (7)$$

The plot of $\ln(q_t/D_0)$ *vs.* $[\alpha\ln\alpha_t+\ln(1-\alpha_t)]$ in Fig. 4 is of (1–*y*) and (1–*x*) is in turn obtained by Eq. (7). As a result, the solid state decomposition kinetic for BPO can then be described by the following equation: $d\alpha_t/dt=k\alpha_t^{0.9}(1-\alpha_t)^{0.5}$

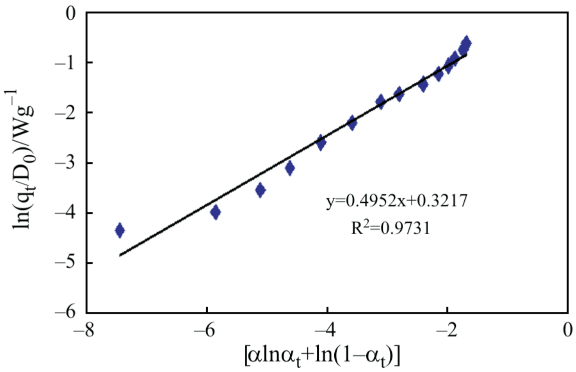

Fig. 4 Determination of reaction order from the slope of $\ln(q_t/D_0)$ *vs.* $[\alpha\ln\alpha_t+\ln(1-\alpha_t)]$

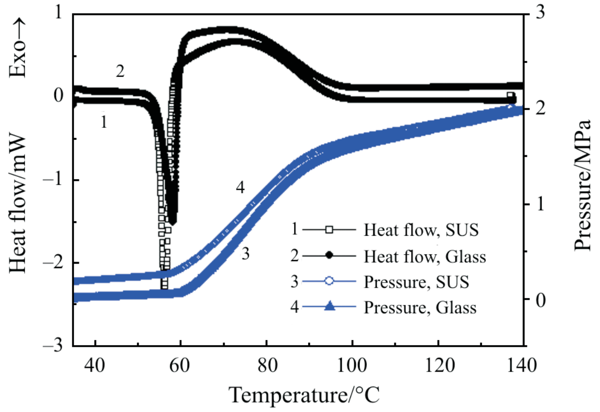

Fig. 6 Non-isothermal reaction curves of LPO (heating rate: 0.1 K min^{-1})

Characteristics of decomposition and kinetic parameters of LPO

The reaction curves of LPO were obtained at several temperatures, like 48, 50, 53, 55, 57, and 60°C in the C80, as shown in Fig. 5. The curves of heat flow and pressure *vs.* temperature in a scanning test of LPO at 0.1 K min^{-1} were drawn in Fig. 6. It is evident from Fig. 6 that under the non-isothermal condition studied, the sample started to melt at 56°C, and the reaction commenced at about 54°C in liquid state as soon as the sample totally melted at about 60°C. Similarly the melting was observed in the isothermal measurement in Fig.5, but melting was detected at lower temperatures (above 48°C) than that in the non-isothermal measurement. After the samples almost melted, heat flow suddenly leaped to the maxima and then they declined exponentially, exhibiting the shape of reactions as *N* order reaction of Eq. (1). As the measured temperature decreased, time taken for the phase transformation and the reaction commence was extended to several days. For example, it took about 0.5 day at 53°C, 3.5 days at 50°C and 11 days at 48°C for melting of LPO, respectively, before a reaction began from a climax at each temperature. The maxima also declined with the decrease of the temperature. Since the appearance of the reaction showed an exponential decay in heat flow and the logarithmic heat flow per unit mass, $\ln(q_t/D_0)$, *vs.* time were demonstrated as straight lines in Fig. 7, the reaction order of LPO can be considered as 1. In this case q_t/D_0 is related to the rate constant and the reaction enthalpy of reaction by Eq. (8).

$$q_t/D_0=-\Delta Hk(1-\alpha_t)=A'\exp(-kt) \tag{8}$$

The slope of $\ln(q_t/D_0)$ *vs.* time is the rate constant. First order reaction is the only case in which the rate constant can be directly obtained by thermal calorimetry [4]. Besides this straight line, a plot of logarithm of the rate constant k *vs.* $1/RT$ is also a straight line, as illustrated in Fig. 8:

$$\ln k=\ln A-E/RT \tag{9}$$

Its slope yields the activation energy in Table 2.

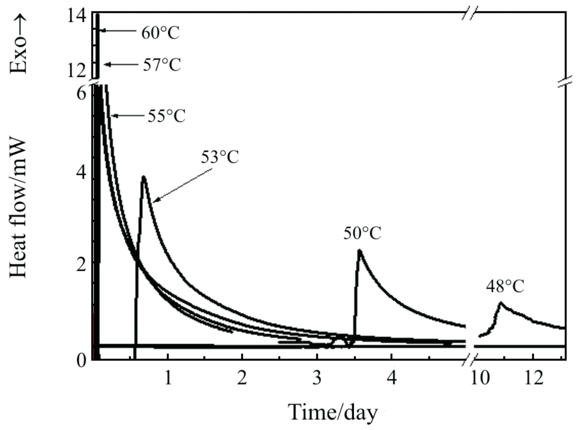

Fig. 5 Isothermal reaction curves of LPO

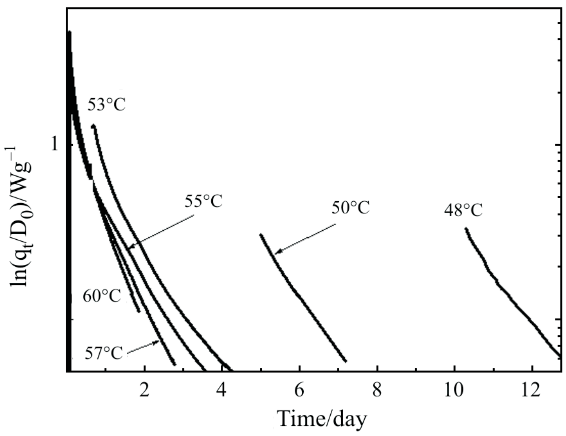

Fig. 7 Determination of reaction order (the reaction of LPO is determined as 1st order)

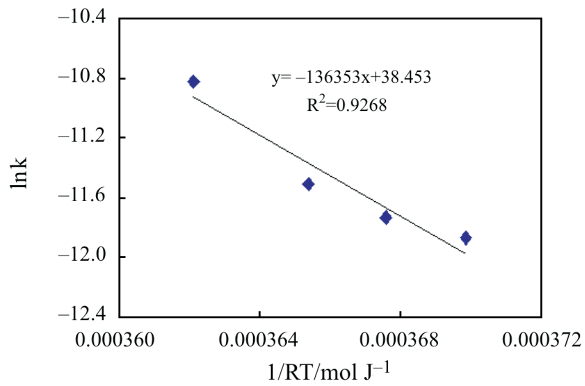

Fig. 8 Determination of activation energy from the slope of ln$k$ *vs*. 1/RT

Characteristics of decomposition and kinetic parameters of ABCN

The reaction curves of ABCN at 83, 85, 87, and 90°C, were shown in Fig. 9 and the corresponding scanning tests were shown in Fig. 10. In the isothermal tests in Fig. 9 the two peaks of heat flow at each temperature apparently indicated that the sample underwent two stages of reaction. As the matter of fact, it is just an autocatalysis of ABCN, similar to what happened in BPO, accompanied by the phase change during melting. Both these effects competed with each other and led to two peaks. The reaction started in solid phase with exothermic effect to the first peak, and meanwhile endothermic melting led the net heat to drop down to a certain degree where a reaction went on, exothermic effect became dominant again and attained to the second peak, and finally the heat flow reduced due to the consumption of the intermediate product. Therefore, the substance underwent a pseudo-autocatalytic reaction, that is, an autocatalytic reaction is accompanied by a physical phase change.

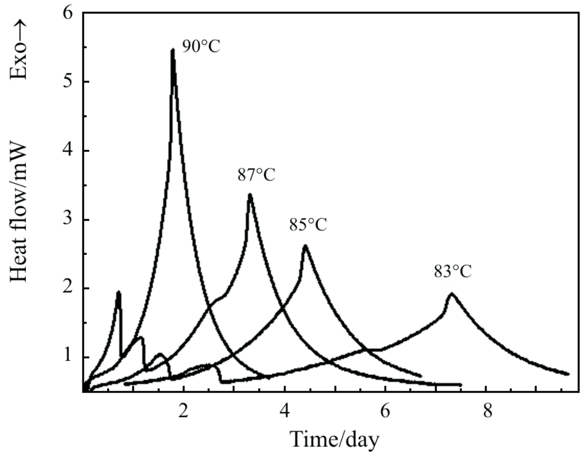

Fig. 9 Isothermal reaction curves of ABCN

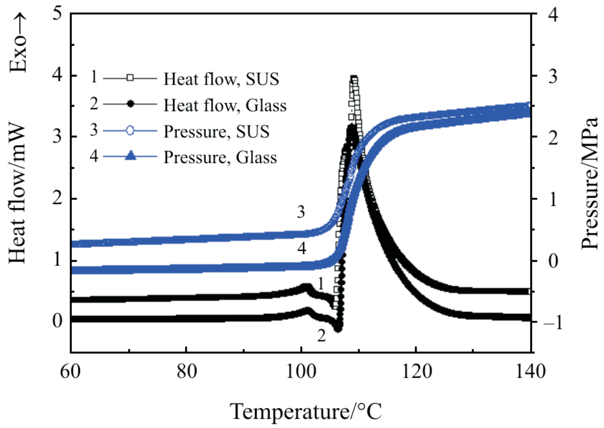

Fig. 10 Non-isothermal reaction curves of ABCN (heating rate: 0.1 K min^{-1})

The melting can also be seen at the beginning of the reaction (from 92 to 107°C) in the scanning measurement in Fig. 10. Pressure slightly increased at about 102°C and the net heat was balanced by the endothermic effect of physical phase change and exothermic effect of chemical reaction. By means of the isothermal method, the complex reaction mechanism of ABCN can be made more clearly. For ABCN, the kinetic calculation is much more complicated. Considering that the first peak was small compared to the

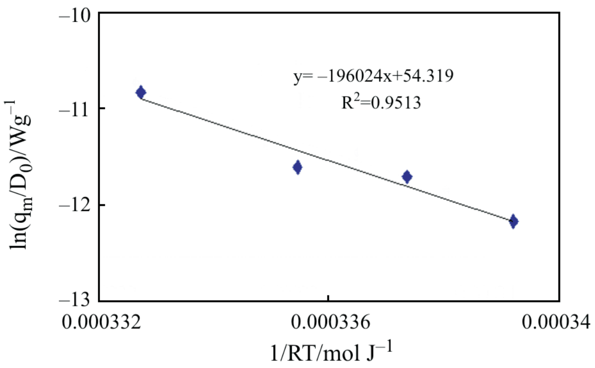

Fig. 11 Determination of activation energy from the slope of ln(q_m/D$_0$) *vs*. 1/RT

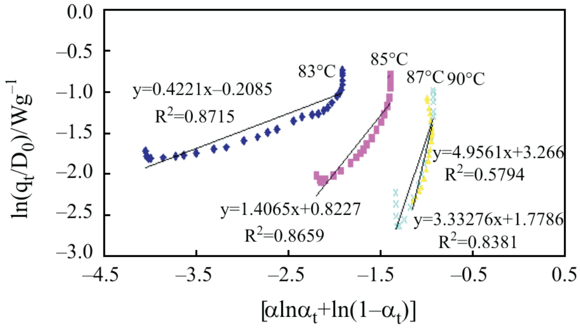

Fig. 12 Determination of reaction order from the slope of ln(q_t/D_0) *vs*. [αlnα_t+ln(1–α_t)]

Table 2 Characteristics of the reactions

Parameter	BPO	LPO	ABCN
Nature of reaction	Solid decomposition	Liquid decomposition	Solid-liquid decomposition
Reaction mechanism	Autocatalytic	Pseudo-first order	Pseudo-autocatalytic
Rate law	$d\alpha/dt=k\alpha^{0.9}(1-\alpha)^{0.5}$	$d\alpha/dt=k(1-\alpha)$	Variables with temperature as in Fig. 12 1–x=0.4, 1–y=0.8 at 83°C 1–x=1.4, 1–y=1.8 at 85°C 1–x=1.6, 1–y=3.3 at 87°C 1–x=2.3, 1–y=4.9 at 90°C
E_a/kJ mol^{-1}	188.0	136.4	196.0
ΔH/J g^{-1}	1072	678	556
ln$A$	60.6	38.4	54.3

second one, it is approximately treated as autocatalytic reaction.

Similar to the case of BPO, from the second maximum linear heat flow and temperature, E and A can be obtained as Fig. 11. And plotting $\ln(q_t/D_0)$ *vs.* $[\alpha\ln\alpha_t+\ln(1-\alpha_t)]$ as in Eq. (6), the reaction order can be estimated, as in Fig.12. It should be noted that the reaction orders are variables of temperature, implying that the reaction is significantly influenced by the melting.

The mechanisms of these three samples are summarized in Table 2. It suggests that the evaluation of a pseudo-autocatalytic reaction like ABCN should be optimized.

Conclusions

In this study, complex reaction schemes occurring near the SADT were characterized by an isothermal method using a calorimeter of high sensitivity. A plenty of quantitative information on the rate laws of different samples, and the related chemical and physical mechanisms were ascertained from the shapes of the heat flow curves. The activation energies of the reactions were determined from the Arrhenius plots. This technique confirmed the decomposition mechanism of self-reactive substances, for which first order, autocatalysis or pseudo-autocatalytic reaction could be recognized.

The isothermal method is also compared with the non-isothermal measurement. The onset temperature of a reaction measured in the isothermal measurement is in the range of its SADT. In contrast this temperature is much higher when tested by non-isothermal ways. Meanwhile, an isothermal way can reveal more evidence on the phenomenon near the SADT. It provides a similar condition and a proper analytical method of studying the complex reaction, in particular for solids near their SADTs during a long storage time.

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