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SADT prediction of autocatalytic material using isothermal calorimetry analysis

Xin-Rui Li*, Hiroshi Koseki

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

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Abstract

Although plant experience is essential, it is possible to assess the hazard of large scale process operation using a logical process based on experimental data. This paper reported an analytical procedure to characterize the reaction and the decomposition kinetics for organic peroxide near its self-accelerating decomposition temperature (SADT) by means of isothermal calorimetric data in a thermal activity monitor (TAM). As a result, a complex reaction where autocatalysis or some physical phenomena may take place was determined. And consequently the SADT in full-scale packages for such an autocatalytical substance was estimated.

Keywords: SADT; Solid; Autocatalysis; Isothermal; Calorimeter

1. Introduction

The self-accelerating decomposition temperature (SADT) is defined as the lowest ambient temperature at which auto-accelerative decomposition of unstable substance occurs. That is, when the self-heating rate of 6 K in a week is observed in the packaged substance in a commercial container the minimum storage ambient temperature reaches the SADT. This temperature is determined for the purpose of deciding whether a self-reactive substance should be subject to temperature control to avoid accident during the transportation. Tests should be conducted in a manner such that the results are representative of the commercial package's material, size and configuration. In order to measure the SADT of organic peroxides four kinds of tests are described in Division 5.2 of the Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria of the United Nations [1]. They are rather desired, however, the recommended test procedures not only can be hazardous to the environment due to the relatively large sample size and the possibility of a violent reaction, but also they need long time to conduct. Therefore alternatively, many analytical evaluations [2–9] have been developed to predict the SADT in a full-scale package from using small-scale experimental measurements by thermal calorimeters.

The principle is based on that the SADT is the critical temperature when the rate of heat generation of a reaction in a given mass exceeds the rate of heat loss from the package to the surrounding. Therefore to evaluate the SADT, it is essential that the kinetic parameter of a chemical reaction should be obtained, from isothermal, non-isothermal and adiabatic reaction calorimeters. The most common apparatus for measuring the SADT is the accelerating rate calorimeter (ARC), an adiabatic reaction calorimeter [2–6]. The general assumptions for the development of thermal explosion models are: (1) homogeneous system; (2) no depletion of reaction (zero-order kinetic); and (3) simple reaction mechanism (single *n*th-order reaction). However it is dangerous to estimate the SADT by extrapolating data obtained by the adiabatic calorimeter and such assumptions, since flagrant errors may be produced if the reaction is not a simple one. To obtain an accurate estimate of the SADT, the mechanism of decomposition must be made clear both chemically and physically. Therefore, the calorimeter must be highly sensitive, at least can detect heat flow of 10–0.1 μW, and

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* Corresponding author. Tel.: +81 422448392; fax: +81 4224448392.
E-mail address: li@fri.go.jp (X.-R. Li).

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we must take into account that such test conditions are to be close to what happens under the real storage conditions at certain ambient temperatures. So an isothermal calorimeter is more appropriate to satisfy such requirements.

An analytical procedure was reported in this paper to characterize the reactions and the decomposition kinetics for an organic peroxide at the temperature range covering its own SADT by means of isothermal method in an isothermal calorimeter, thermal activity monitor (TAM), in order to clarify the reaction mechanism of the desired sample. Feasible kinetic was consequently analysed, and laid a theoretical foundation for the SADT evaluation under the assumptions of the physical model of Frank-Kamenetskii in a 500 ml Dewar vessel test and in a USA SADT test.

2. Experiments

An isothermal calorimeter, Multi-channel Microcalorimetry System 2277 (TAM, Thermometric AB, Sweden), was used for the purpose of determining both what type of decomposition reaction is occurring (the reaction mechanism) and the kinetic of the reaction. All channels are placed in a water bath in the TAM which is finely controlled to be at the set temperature by a series of thermostats. The whole system is therefore kept at a constant temperature (isothermal).

Benzoyl peroxide (BPO) was chosen as a sample and placed in a stainless steel vessel that was lowered into the central channel. The heat flows from a studied reaction to the heat sink (water bath) and vice versa from the heat sink to the reaction site were measured. The thermopiles that measured the heat flow of the reaction were extremely sensitive and were capable of measuring a reaction with a heat flow of at least 10 μW. Benzoyl peroxide was granular solid, containing 25% water. Two hundred milligrams of BPO was set in the TAM at 65, 70, 72, and 75 °C to carry out the measurements.

3. Results and discussion

3.1. Results

The reaction curves of BPO were obtained in the TAM at several constant temperatures, as shown in Fig. 1. The reaction, whose heat generation was detected above 70 °C, occurred in solid state, since no endothermic effect was observed at each temperature. In each reaction curve, at first heat flow increased, and after reaching a maximum it decreased. The shape of the reaction curves is characteristic of an autocatalytic reaction at all temperatures studied [9–13]. The mechanism can be explained as below.

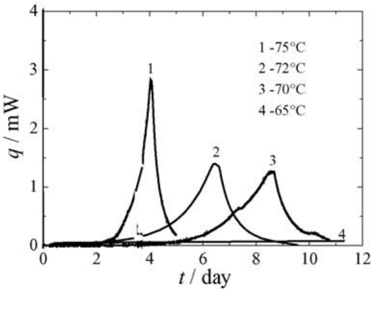

Fig. 1. Reaction curves of BPO in the TAM, 200 mg.

The thermal decomposition of organic peroxides is comprised of two main elements [13]:

(1) Homolysis of the O–O bond

$$[(RCO_2)]_2 \rightarrow 2RC(O)\text{–}O^{\bullet}$$

(2) Radical-induced decomposition

$$[(RCO_2)]_2 + R'^{\bullet} \rightarrow R\text{–}C(O)\text{–}O\text{–}R' + 2RC(O)\text{–}O^{\bullet}$$

It is not easy to determine how much each of the modes contributes to the overall process of thermal decomposition of any peroxide. Generally speaking, aroyl peroxides are easier subject to free-radical attack at O–O aliphatic analogs. Species which have saturated bond, like phenyl in BPO, tend to increase the rate of decomposition (i.e., faster production of the radical). This is due to the stabilization of the electron cloud for the free radical species [14]. In benzoyl peroxide, PhC(O)–O$^{\bullet}$ tends to be a more stable radical and act as potential nucleus forming sites in the subsequent reaction, and in turn oxygen–oxygen bond of benzoyl peroxide is attacked by ester radicals and reacts with them. If this reaction proceeds intensely, the peroxide is decomposed by the free radicals. The overall effect of formation and depletion of the free radicals therefore leads to autocatalysis effect in the reaction. The final products of decomposition of BPO are carbon dioxide and biphenyl, and also smaller amount of phenyl benzoate and benzene are produced. In comparison, first-order decomposition was measured in an analogical diacyl peroxides, *tert*-butyl peroxide $[(t\text{-butylCO}_2)]_2$ [15], indicating that only homolysis occurs in this sample, which leads the reactant to be consumed monotonously.

3.2. Kinetics of benzoyl peroxide

As mentioned above, induced decomposition such as an autocatalysis is a process which generates free-radicals, thus the reaction rate is characterized by the apparent change of the free-radical in this type of decomposition. The followings describe how kinetic can be derived from decomposition heat flux.

D_0 is defined as the amount of sample at the time $t = 0$, and β is defined as the fraction of the peroxide which ultimately react. α_t is defined to be the conversion ratio, that is, the fraction of the reaction which has occurred to time t, i.e., $\alpha_t = 0$ at $t = 0$ and $\alpha_t = 1$ at $t = \infty$. The converted reactant which has decomposed at the time t is given by $\alpha_t \beta D_0$. The value of α_t as obtained from calorimetric data is given by Eq. (1),

$$\alpha_t = Q_t/Q_\infty \qquad (1)$$

where Q_t is the total heat produced to the time t and Q_∞ is the total heat produced to $t = \infty$, being equal to the enthalpy of the reaction, ΔH. Thus, Eq. (2) can be obtained:

$$Q_t = -\Delta H \alpha_t \beta D_0 \tag{2}$$

The Q_t can be obtained by a numerical integration of heat flow q from $t = 0$ to any t and the value of Q_∞ can be obtained likewise by integration of the entire q–t curve in Fig. 1. Differentiation of Eq. (2) gives the relation between q_t, the rate of heat change ($\mathrm{d}Q_t/\mathrm{d}t$), and the rate of the reaction ($\mathrm{d}\alpha_t/\mathrm{d}t$) in Eq. (3):

$$\mathrm{d}Q_t/\mathrm{d}t = q_t = -\Delta H \beta D_0 (\mathrm{d}\alpha_t/\mathrm{d}t) \tag{3}$$

Since $\mathrm{d}\alpha_t/\mathrm{d}t$ is equal to the product of the rate constant, k, and some function of α_t, $f(\alpha_t)$, the next part of the problem is to find $f(\alpha_t)$, which correctly describes the experimental q–t data for a given case. Jocobs derived the feasible kinetic forms based on the theory of nucleation and nucleus growth [10]. The factor of $f(\alpha_t)$ depends on the reaction mechanism, as well as topochemical and geometry of the reactive particles. Ng et al. [10–13,16,17] has shown that the rate of a reaction may be expressed in general by the function of α_t given in Eq. (4):

$$\mathrm{d}\alpha_t/\mathrm{d}t = k\alpha_t^{1-x}(1-\alpha_t)^{1-y} \tag{4}$$

where x and y are the constants characterizing the reaction mechanism. k is the rate constant. When substituting Eq. (4) into Eq. (3), Eq. (5) is obtained:

$$q_t/D_0 = -\Delta H \beta k \alpha_t^{1-x}(1-\alpha_t)^{1-y} \tag{5}$$

In the case of autocatalytic kinetics, x is related to the accelerating phase of the reaction and y is related to the decelerating phase. To determine the reaction orders of $1-x$ and $1-y$, it can be shown that at $q_{\max}$, the point in time when the maximum heat rate is observed, $\mathrm{d}[\mathrm{d}\alpha_t/\mathrm{d}t]_{t=t_\mathrm{m}} = 0$, and thus Eq. (6) applies from differentiation of Eq. (5):

$$\alpha_\mathrm{m}/(1-\alpha_\mathrm{m}) = (1-x)/(1-y) = a \tag{6}$$

$$\alpha_\mathrm{m} = (1-x)/(2-x-y) = Q_\mathrm{m}/Q_\infty \tag{6a}$$

where α_m and Q_m are the conversion ratio and heat production respectively when the maximum heat rate is observed. a is the constant of ratio of the reaction order. Eqs. (6) and (6a) show how the values of a and α_m are obtained from the calorimetric data. The value of Q_m can be obtained by numerical integration of q from $t = 0$ to t_m. Substituting Eq. (6) into Eq. (5) results in Eq. (7):

$$q_t/D_0 = -\Delta H \beta k [\alpha_t (1-\alpha_t)^{1/a}]^{1-x} = C[\alpha_t(1-\alpha_t)^{1/a}]^{1-x} \tag{7}$$

Eq. (7) can be expressed in logarithmic form as

$$\ln(q_t/D_0) = \ln C + (1-x)[\ln\alpha_t + 1/a(1-\alpha_t)^{1/a}] \tag{7a}$$

where C is the constant. The logarithmic form of Eq. (7a) results in directly informative linear plots if $\ln(q_t/D_0)$ is plotted as the ordinate and a proper function of time is plotted as the abscissa, as in Fig. 2. The intercept of such a plot contains the information on ΔH, β and k for the reaction, but these constants are not separable in isothermal data. The slope of such a plot, however, contains sufficient information to quantify the rate law. As seen in Fig. 2, the slopes at the temperatures studied in the paper (70, 72, and 75 °C) are all same, indicating that the reaction order keeps consistent and reaction scheme of BPO does not change within this temperature range. As a result, the solid state decomposition kinetics for BPO in Eq. (4) can then be correspondingly described by the following Eq. (8)

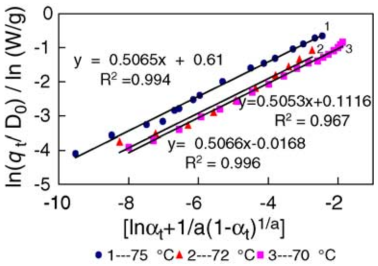

Fig. 2. $\ln(q_t/D_0)$ vs. $[\ln\alpha_t + 1/a(1-\alpha_t)^{1/a}]$ of benzoyl peroxide (the slope is the value of $1-x$).

$$\mathrm{d}\alpha_t/\mathrm{d}t = k\alpha^{0.9}(1-\alpha)^{0.5} \tag{8}$$

The temperature dependence of the rate law of a reaction may also be obtained by determining q–t curves at several temperatures. With a fairly narrow temperature range, the Arrhenius equation given in Eq. (9) is used to describe the temperature dependence of the rate law assuming that only one rate-limiting reaction presents

$$k = A\exp(-E/RT) \tag{9}$$

A is the pre-exponential factor, R is the gas constant and, E is the activation energy, and T is the absolute temperature. The activation energy for an autocatalytic reaction can be obtained from the q_m vales at different temperatures

$$q_\mathrm{m}/D_0 = -\Delta H \beta k \alpha_\mathrm{m}^{1-x}(1-\alpha_\mathrm{m})^{1-y} = A' \exp(-E/RT) \tag{10}$$

where q_m is the value of heat flow when the rate of the reaction is maximum. Thus, a plot of $\ln(q_\mathrm{m}/(D_0 \Delta H \beta k))$ against $1/RT$ in Fig. 3 will be linear and have a slope of $-E$.

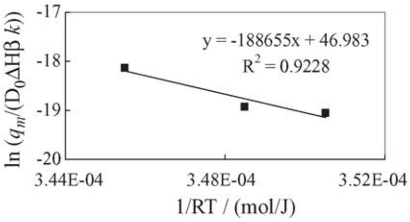

Fig. 3. $\ln(q_\mathrm{m}/(D_0 \Delta H \beta k))$ vs. $1/RT$ of benzoyl peroxide (the slope is the value of activation energy).

Table 1
Characteristics of the reactions and obtained SADT by various ways

Sample	BPO
Nature of reaction	Solid decomposition
Rate law	Autocatalytic
Activation energy (kJ/mol)	188.6
Evaluated SADT (°C)	
In Dewar	72
In 25 kg package	73.5
Reference SADT (°C) [22] in Dewar	<75

3.3. *Determination of the SADT in large scale package*

The SADT has been designed to deal with the scale-dependence problem for a given unstable substance. It is determined by experimental measurement or by calculation based on the thermal explosion theory. Knowledge of the SADT of thermally unstable chemicals is vital for the prevention of ignition or explosion incidents which such chemicals bring about. For liquids in homogeneous systems throughout the masses, the Semonov critical condition is applied [3,4,8,15,18]. On the other hand, for solids, it has been already well confirmed that the value can be determined by applying the Frank-Kamenetskii thermal explosion model [5,7,9,19–21]. It was derived from the assumption that the temperature distribution in solid is inhomogeneous. Thus a critical Frank-Kamenetskii parameter, δ_c, is expressed as follows:

$$E/RT_A^2 \Delta HA/\lambda \exp(-E/RT_A)\rho[C]^n = \delta_c \tag{11}$$

where T_A is the ambient temperature and equals to the SADT corresponding to δ_c. λ is the reactant thermal conductivity (0.09 W/K/m for BPO), C is the reactant concentration, and n is the reaction order. δ_c is 2.0 for the Dewar vessel and 2.78 for the 25 kg package.

According to previous papers, reactant consumption was negligible around the SADT [2–8]. The reason was that at the SADT, the reaction was thought to undergo at an initial induction time when the mass of the consumed reactant is fairly small compared to the total initial reactant mass. However, in the case of autocatalysis occurring in benzoyl peroxide, the conventional assumptions should be revised: reactant is inevitably depleted over nearly 1 week and the reactant depletion is significant; the reaction is autocatalysis and hence $[C]^n$ is substituted by Eq. (8).

The results in Table 1 show that the SADT can be estimated accurately, provided kinetic data are enough reliable.

4. Conclusions

We obtained the following conclusions:

(1) It is dangerous to estimate the SADT by extrapolating data obtained from a non-simple reaction. To obtain an accurate estimate of the SADT, the mechanism of decomposition must be made clear both chemically and physically.
(2) To determine the feasible reaction kinetic, isothermal measurement and high sensitivity of the calorimetry were essential to use. Consequently a correct kinetic to fit the character of the reaction in particular for the autocatalysis was obtained. Reaction of benzoyl peroxide was described by this procedure. Its thermal decomposition is autocatalysed by the free radical.
(3) After clarifying the chemical and physical natures of the solid, the Frank-Kamenetskii model is applied to extrapolate the data to large size container, in order to estimate the SADT in full-scale packages. Meanwhile reactant depletion should be considered when determining SADT value in case of a highly exothermal reaction of benzoyl peroxide.

References

[1] The United Nations, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria of UN, 4th ed., New York, 2003, pp. 249–260.
[2] D.I. Townsend, Thermochim. Acta 37 (1980) 1–30.
[3] M.W. Whitmore, J.K. Wilberforce, J. Loss Prevent. Process Ind. 6 (1993) 95–101.
[4] H.G. Fisher, D.D. Goetz, J. Loss Prevent. Process Ind. 4 (1991) 305–316.
[5] H.G. Fisher, D.D. Goetz, J. Loss Prevent. Process Ind. 6 (1993) 183–194.
[6] S. Mores, P.F. Nolan, G.O. Brien, IChemE Symp. Ser. 134 (1994) 615–627.
[7] P.H. Thomas, Trans. Faraday Soc. 54 (1968) 60–65.
[8] Y. Yu, K. Hasegawa, J. Hazardous Mater. 45 (1996) 193–205.
[9] K. Hasegawa, Y. Li, Proceedings of the Ninth International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Barcelona, Spain, 1993, pp. 555–569.
[10] P.W.M. Jacobs, in: J.W. Mitchell, et al. (Eds.), Reactivity of Solids, John Wiley, New York, 1969, pp. 207–218.
[11] W.L. Ng, Aust. J. Chem. 28 (1975) 1169–1178.
[12] R.J. Willson, A.E. Beezer, J.C. Mitchell, Int. J. Pharmaceut. 132 (1996) 45–51.
[13] I. Halikia, L. Zoumpoulakis, E. Christodoulou, D. Prattis, Eur. J. Miner. Process. Environ. Protect. 1 (2) (2001).
[14] R. Hiatt, in: D. Swern (Ed.), Organic Peroxides, vol. II, Wiley/Interscience, 1971, pp. 812–815.
[15] X.R. Li, H. Koseki, International Conference on the 20th Anniversary of the Bhopal Gas Tragedy, India, December 1–3, 2004.
[16] T. Ozawa, J. Therm. Anal. 2 (1970) 301–324.
[17] T. Ozawa, Thermochim. Acta 203 (1992) 159–165.
[18] N.N. Semonov, Some Problems of Chemical Kinetic and Reactivity, Part II, Pergamon Press, London, 1959.
[19] D.A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetic, 2nd ed., Plenum Press, NY, 1969.
[20] J.H. Sun, X.R. Li, K. Hasegawa, G.X. Liao, J. Therm. Anal. Calorimetry 6 (2004) 883–893.
[21] X.R. Li, H. Koseki, Proceedings of the 11th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Praha, Czech Republic, May 31–June 3, 2004, pp. 2278–2285.
[22] Nippon Oil & Fats Co., LTD. (NOF), Organic Peroxide, fourth ed., Technical note of NOF, Tokyo, Japan, 17 pp.