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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

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.
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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 nth-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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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 $10\,\mu W$. Benzoyl peroxide was granular solid, containing 25% water. Two hundred milligrams of BPO was set in the TAM at 65, 70, 72, and $75\,^\circ C$ 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
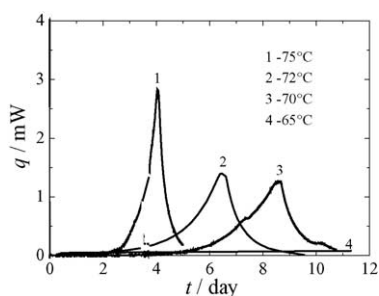

Fig. 1. Reaction curves of BPO in the TAM, 200 mg.

reaction, whose heat generation was detected above $70\,^\circ C$, 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.

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

(1) Homolysis of the O–O bond

$$[(RCO_2)]_2 \rightarrow 2RC(O)-O^\bullet$$
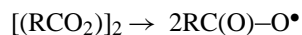
(2) Radical-induced decomposition

$$[(RCO_2)]_2 + R'^\bullet \rightarrow R-C(O)-O-R' + 2RC(O)-O^\bullet$$
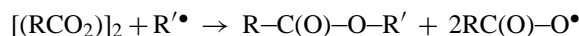
It is not easy to determine how much each of the modes contributes to the overall process of thermal decomposition of any peroxide. Generally speaking, aroyl peroxides are easier subject to free-radical attack at O–O aliphatic analogs. Species which have saturated bond, like phenyl in BPO, tend to increase 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),

$$\alpha_t = Q_t/Q_\infty \tag{1}$$