Study on thermal decomposition characteristics of AIBN

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Abstract

It is found that the results such as observed in the differential scanning calorimeter (DSC), which show the major thermal decomposition (TD) of a self-reactive material, lack the detail to reveal what happens at the initial stage of a reaction. The reaction at this stage is corresponding to the handling condition of storage or transportation, often possibly having the potential to be developed to a runaway reaction. This paper examined and compared the thermal behaviors of AIBN at various working conditions in calorimeters and Dewar vessels. The mechanism that affects the initial reaction and self-heating behavior of the given material was clarified. Near its onset decomposition temperature, physical processes, such as sublimation or melting interfered the initial reaction of AIBN. The mutuality of the physical effect and the chemical reaction made AIBN behave differently under different measuring conditions, and as the result, quasi-autocatalysis or TD possibly occurs in the same sample at the handling temperature range. The heat accumulation storage tests in two Dewar vessels presented completely different self-heating behaviors due to this mechanism and heat transfer capability of the vessels.
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1. Introduction

AIBN (2,2′-azobis (isobutyronitrile)), widely used for blowing agent and initiator, is a typical self-reactive material. Being azo compound, it belongs to class 5 in the UN classification, having risk to runaway due to its self-heating during storage or transportation. Self-heating normally is started from the early stage of a reaction progress, such as near its SADT (self-accelerating decomposition temperature), a critical onset temperature of thermal explosion.

The characteristic of a complex reaction, being presented by the change of the concentration of reactants, is not easily found by direct chemical way. Generally there are two alternative two methods to characterize the type of a decomposition of organic peroxides, self-reactive materials and explosives. One is by means of thermal analysis, mostly at isothermal conditions: the rate of heat production in a reaction is proportional to the rate of the reaction since all physical and chemical processes are accompanied with heat exchange [1–5]. If the reaction is basically accelerated by temperature increment and thus the rate of reaction depends only upon the temperature, it follows a N order rate law, that is, at a certain temperature the heat flow leaps to the maxima at the beginning of the measurements and then it declines exponentially, this reaction is characterized as thermal decomposition type (TD type)—the reactant decays to exponentially form the product; whereas if at the initial stage some amount of the product is generated and then it may in turn trigger self-acceleration, the scheme of the reaction represents the model of autocatalysis (AC type). At a certain temperature, an intermediate free radical which is auto generated causes the rate of reaction, as well as heat flow, to increase gradually until reaching the climax. During this stage the intermediate free radical behaves as product, whose concentration is rising in value, though its generation and consumption are simultaneously happening all the time. After the climax is reached the consumption of the intermediate product tends to be dominant and the heat flow decreases with the time. In addition to the above two schemes, for solids there is a 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.

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Table 1
Measurements of AIBN

Apparatus	Cell	Sample	Conditions
DSC8230 (Rigaku)	Al cell sealed	2–5 mg	At 0.5, 2, 2.5, 5, 10 and 20 K/min
TG–DTA (Rigaku)	Al cell open	2–5 mg	At 0.5, 2, 2.5, 5, 10 and 20 K/min
HPDSC[a] (Mettler Toledo)	Al cell in N_2	10 mg	At 10 K/min
C80 (Setaram)	SUS cell sealed	0.5 g[b]	At 0.01 and 0.1 K/min; isothermal: 57, 59, 62 and 64 °C
Dewar vessel[c]	500 ml, cylinder	260 g	Ambient temperature: 45 °C (no self-heating) and 50 °C (runaway)
Dewar vessel[c]	1000 ml, sphere	490 g	Ambient temperature: 40 °C (no self-heating) and 45 °C (runaway)

[a] HPDSC: high pressure DSC.

[b] Besides AIBN, its solutions in acetone (20%) and in toluene (4%) were also measured at 0.1 K/min in the C80.

[c] Based on the BAM test (H4) [2], temperature distribution measurement inside of vessel was done.

The other means is to classify the type of a decomposition or reaction in self-heating measurements. Kotoyori classified the self-heating properties of a chemical, charged in open-cup cell or confined in the closed cell, into two similar groups [6]. TD type exhibits that when being warmed up to the surrounding temperature, the rate of heat generation of the chemical exceeds the rate of heat transfer from the chemical to the surrounding throughout the whole self-heating process, with the result that the temperature of the chemical continues to increase acceleratedly until the ultimate runaway happens; On the other hand, for an AC type, when being warmed up to the surrounding temperature, the chemical does not continue to self-heat over, but remains at the surrounding temperature for a long time. In the meantime the decomposition reaction of the chemical to generates an autocatalyst proceeds very slowly. The final runaway happens when all autocatalyst is produced.

AIBN is basically taken as a TD type material of decomposition based on the TG–DTA (thermogravimetry/differential thermal analysis) or DSC (differential scanning calorimeter) data [6–9]. However, there is still much ambiguity because contradictory information came from different measurements and as a consequence led to misleading description of the overall decomposition process. In particular few studies concerned the early stage of its reaction which develops self-heating. To get a comprehensive understanding, this paper compared the phenomena related to the thermal decomposition of AIBN in various thermal analysis apparatuses and clarified the reason causing diverse results in different measurements. Subsequently heat accumulation storage test was employed in two Dewar vessels for determining characteristics of AIBN during its self-heating at its critical storage temperatures, and as well as the corresponding temperature profile inside the vessel. A 500 ml cylindrical Dewar vessel, filled with 400 ml of substance, with a heat loss of 80–100 mW/kg K, was used for presenting a 50 kg package [10]. Meanwhile, an 1000 ml spherical Dewar vessel, with lower heat transfer capacity was also used for comparison [11].

2. Experimental

Measurements performed on AIBN in various apparatuses, are listed in Table 1. To evaluate the effect of heating rate on the decomposition of AIBN, temperature ramp measurements at a series of heating rates, 0.5, 2, 2.5, 5, 10 and 20 K/min, were carried out in a DSC (differential scanning calorimeter)

with closed cells and a TG–DTA with open cells, respectively. An HPDSC (high pressure DSC) was also used to compare its decomposition in nitrogen atmosphere at 10 K/min.

A Calvet calorimeter, C80 was used for precise determination of the thermal activities of AIBN. Very low temperature ramp rates, like 0.1 and 0.01 K/min, which are very close to the natural storage situation, were applied in this experiment. Under such conditions, faint initial reaction was possibly able to be detected. The sample of 1 g was filled into the stainless steel vessel of 12 ml. In order to separate the physical effect from the chemical reaction, besides AIBN, its solutions in acetone (20%) and in toluene (4%) were also measured at 0.1 K/min in the C80. As well, several isothermal measurements were performed at temperatures chosen closely to the referenced SADT value, which is recorded as 50 °C in a 500 ml Dewar vessel.

As referred in the UN manual [2], heat accumulation storage test determines the self-accelerating decomposition temperature which is defined as the lowest temperature at which self-accelerating decomposition may occur with a substance in the package as used in transportation. The effectiveness of the method depends on selecting a Dewar vessel with heat loss per unit mass characteristics similar to the package offered for transport. For example, a 500 ml cylindrical corresponds to a package of about 50 kg and whereas an 1000 ml spherical one to 200 kg. The temperature profiles of AIBN during self-heating were carried out in this study by using these two vessels, at corresponding
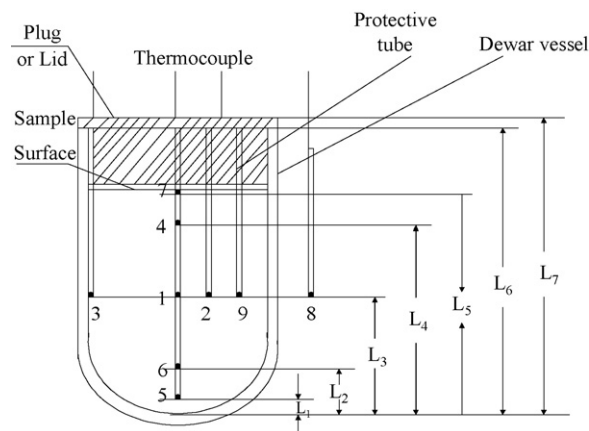

Fig. 1. Scheming construction of measuring system of the cylindrical Dewar vessel (500 ml) (L_1, 10 mm; L_2, 40 mm; L_3, 80 mm; L_4, 120 mm; L_5, 150 mm; L_6, 196 mm; L_7, 200 mm; φ, 65 mm).
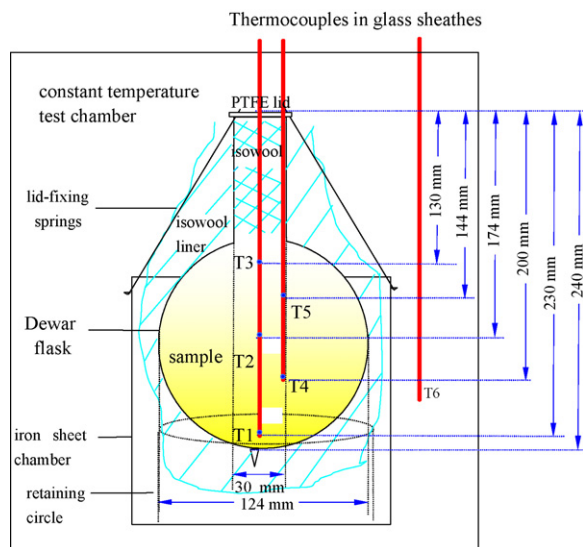
Fig. 2. Scheming construction of measuring system of the spherical Dewar vessel (1000 ml).

critical temperatures in each vessel. The constructions of measuring systems, including the dimension of the thermocouples are schematically drawn in Figs. 1 and 2. In the measurements, four-fifth volume of sample was filled in the vessels and the vessels were equipped with K type thermocouples to measure the temperature profile at different positions in the sample. The surrounding temperature was set at the lowest temperature at which the sample inside exceeded the test chamber temperature and underwent the final runaway reaction. Below this temperature, no self-heating was found, as in Table 1.

3. Results and discussion

3.1. General interpretation of AIBN thermal decomposition

Typical pattern of AIBN decomposition curve has been reported based on the results at 2.5 or 10 K/min in the DSC and TG–DTA in many references [6–9]. Kinetics mainly was obtained based on these results.
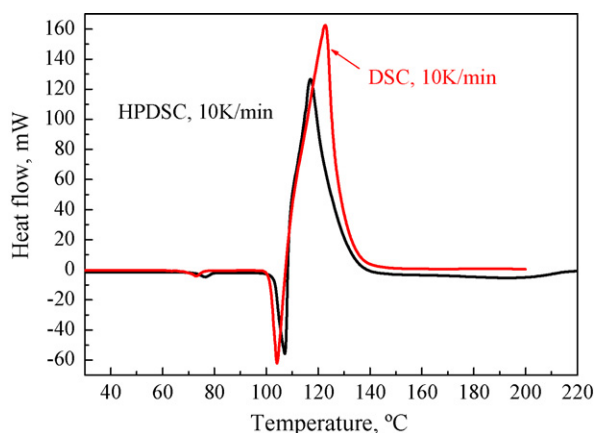

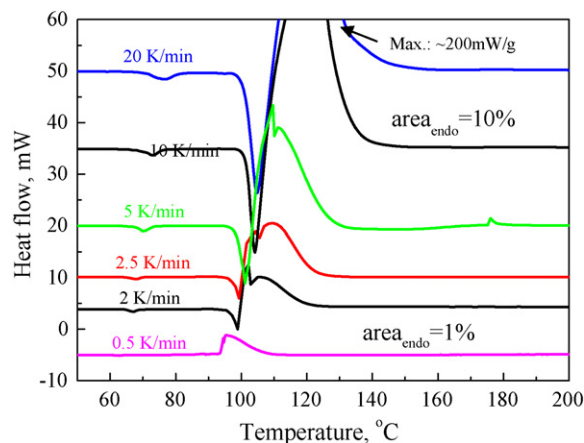Fig. 3. AIBN at 10 K/min in the DSC and HPDSC.

Fig. 4. AIBN at different heating rate in the DSC.

Here these results at a heating rate of 10 K/min in the DSC and HPDSC are also included in Fig. 3. As seen, with the temperature increasing to 70–80 °C, a small endothermic peak appeared, which comes from the phase transition in the AIBN crystal. A second visible endothermic peak appeared at 102–105 °C, and it is usually considered as the melting of AIBN to liquid. And subsequently the major reaction happened at about 110 °C soon after the physical transition. The decomposition behaved as a single exothermic peak and is hence concluded as TD type—the decomposition is apart from its melting and happens in liquefied state. The thermal decomposition of AIBN measured in the HPDSC was not as vigorous as in the DSC. The reason might lie in different measuring atmosphere, which was N_2 in the HPDSC whereas air in the DSC.

3.2. Performance of AIBN near the SADT

It is found in Fig. 4 that the reaction process of AIBN in the DSC changed with the heating rate decreasing. The decomposition of AIBN tended to start at lower temperatures when the heating rate was lowered down (for example it started at 100 °C in the case of 2.5 K/min), and meanwhile the pattern of reaction tended to divide into two peaks below 2.5 K/min. At 0.5 K/min, the onset reaction already crossed ahead to the melting range
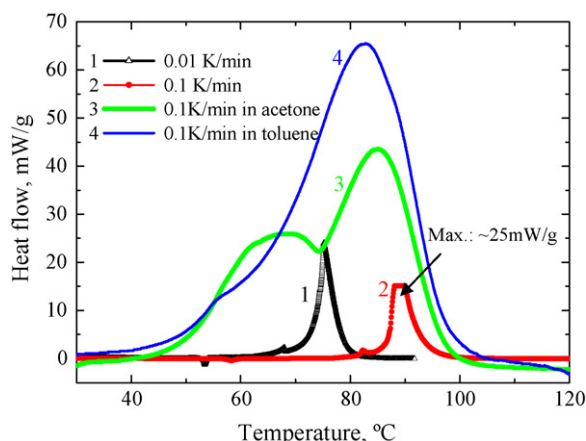

Fig. 5. Temperature ramp measurements of AIBN and its solutions in the C80.
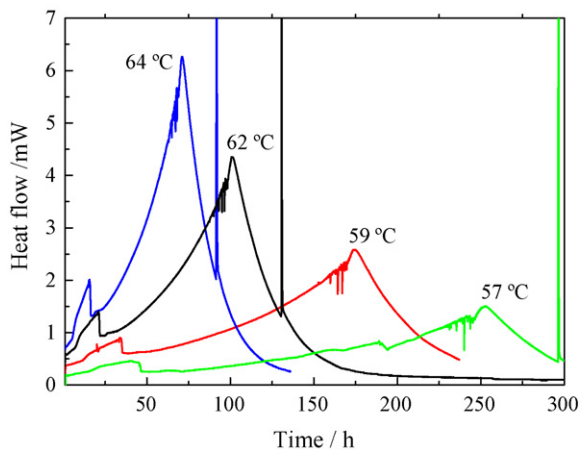
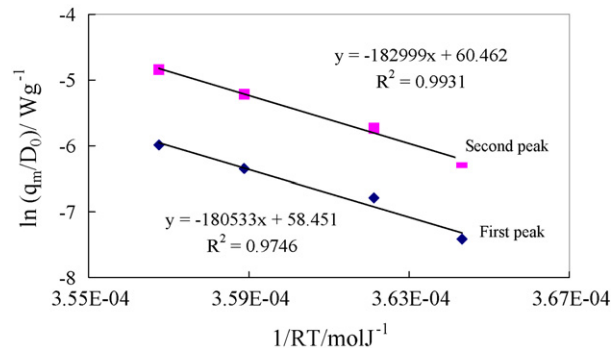Fig. 6. Isothermal measurements of AIBN in the C80.

Fig. 7. $\ln(q_m/D_0)$ vs. $1/RT$ based on Fig. 6, slopes are the value of activation energy, E ((q_m/D_0) is the heat flow per unit mass, R the gas constant and T is the absolute temperature).

and as a result the endothermic peak was covered. This is seen more clearly at heating rates of 0.1 and 0.01 K/min in the C80, as in Fig. 5. In these experiments, the reaction started at much lower temperatures. Physical phase transition, instead of forming a negative heat flow peak, overlapped with the exothermic effect which started at about 60 °C and resulted in two positive heat flow peaks.

In order to observe the 'pure' decomposition behavior, the effect of the physical phase transition was hoped to be obviated. For this purpose, AIBN was dissolved by 20% in acetone and by 4% in toluene, respectively, and was measured at 0.1 K/min in the C80. Results are also shown in Fig. 5. In acetone, decomposition of AIBN showed a two-step reaction, whereas in toluene solution it tended to be an one-step reaction, though with a slight shoulder at 55 °C. Because AIBN was readily separated from acetone when acetone evaporated at elevated temperatures, its decomposition still remained the solid style of decomposition. While it was thoroughly solved in toluene, for which it enabled to reflect the liquid style of decomposition.

The feature of decomposition of AIBN near its SADT (it is 50 °C in a 500 ml Dewar vessels) should be confirmed by the isothermal measurements, as shown in Fig. 6 in the C80. Two saddle shaped peaks of heat flow at each temperature in the range of 57–64 °C apparently implied that the sample underwent two stages of reaction. However, as the matter of fact, it is just one reaction process in parallel with the phase change during melting. Moreover, this was proved by means of analyzing the kinetics of AIBN of these two peaks. From the slopes when plotting the curves of the logarithm of maximum heat flow the two peaks versus the reciprocal of the absolute temperature, the values of the activation energy, E, were obtained as in Table 2

Table 2
Determination of activation energy from $\ln(q_m/D_0) = \ln A - E/RT$ [1,2]

	Temperature, T (°C)			E (kJ/mol)
	64	62	59	
Maximum heat flow, q_m (mW)				
First peak	6.32	4.34	2.56	180
Second peak	1.84	1.46	0.94	183

and Fig. 7 [1–4]. It is noted that the activation energies of the two peaks are the same, implying that these two peaks resulted from a same reaction mechanism. The shape of the heat flow curves are characteristics of autocatalysis [1], AC type of decomposition, in which an intermediate free radical which was auto generated caused the heat flow, to increase gradually until reaching the climax. During this stage the intermediate free radical behaves as product, whose concentration is 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. This result is consistent with that in toluene solution, at the temperature ramp condition, in which the slight shoulder at 55 °C in toluene might be related to the happening of the autocatalysis. For AIBN, the reaction started in solid phase, which was accompanied with the exothermic effect, and meanwhile endothermic melting inhibited the reaction and led the net heat to drop down to a certain degree. But the reaction was auto catalyzed and thus with the reaction going 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. It can be seen that before reaching the second climax, the heat flow fluctuated frequently because the endothermic and exothermic effects still competed with each other even when the reaction became active. Therefore, a quasi-autocatalytic reaction, that is, autocatalytic reaction with parallel to a physical phase transition, happened in AIBN at this stage.

The physical process during AIBN decomposition is also uncertain so far and is needed to be made clear. To this end, TG–DTA was performed at several heating rates. As seen in Fig. 8, an endothermic peak appeared at 116 °C and a subsequent exothermic reaction was observed at about 125 °C under 10 K/min in the DTA. Heat loss on the TG already happened when the endothermic effect started, while it turned significantly when the exothermic process started on the DTA. The lower the heating rate, the more the reaction faded on the DTA curves. At 0.5 K/min, there was a great weight loss on the TG curve from 60 °C, but meanwhile no heat flow was observed on the DTA curve. The exotherm of decomposition might be balanced by the endothermic of sublimation. This implies that at the open condition in the TG–DTA, sublimation, instead of melting of
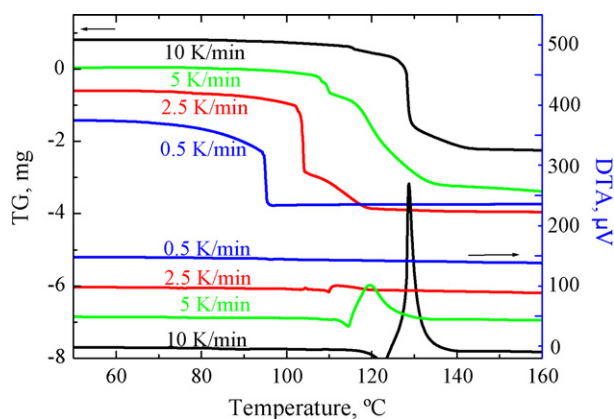
Fig. 8. AIBN in the TG–DTA.

Fig. 9. Temperature profile of AIBN in the 500 ml cylinder Dewar.

AIBN, happened before its reaction. The lower the heating rate, the more dominant sublimation interfered the initial reaction. In general, the kinetic analysis and classification of self-reactive chemicals may be based on the TG–DTA (open cell) data, but it was less valuable because in the open system the evaporation or sublimation may affect the results.

It seems that the onset temperature of the chemical reaction of AIBN shifts, dependent upon its working condition. If physical phase transition of AIBN just happens in the area of its initial reaction, it makes the phenomenon of AIBN reaction more complicated, and usually unclear for observing. Endotherm absorbs part of the heat of first step reaction, and as a result of the competence between the exothermic and endothermic effects, various possibilities may take place: (1) the endothermic peak appears prior to its major thermal decomposition at higher heating rate, and hence the decomposition happens in liquid or gas phase; or (2) the endothermic effect is wedged to the decomposition of AIBN to form two saddled exothermic peaks at lower heating rate or isothermal conditions, and the decomposition is more likely occur at in liquid–solid phase.

3.3. Behaviors of self-heating in Dewar vessels

The above results help to explain the phenomena of AIBN in the Dewar vessels. It is seen that the behaviors of self-heating of AIBN were quite different in the cylindrical and spherical Dewar vessels.

In the cylindrical Dewar vessel in Fig. 9, the critical temperature for runaway of AIBN was 50 °C. This temperature right lay at the point of sublimation or melting. The temperature inside the sample was warmed up and attained the same value of the surrounding temperature after 20 h, and then it turned down owing to the heat absorption by its physical state change over 50 h. From then on the temperature did not continue to be self-heated over, but remained at the surrounding temperature for a long time. This is because that AIBN underwent generating an autocatalyst and it proceeded very slowly during this induction period. After about 200 h, once the concentration of the autocatalyst attained to a definite threshold value, the process to generate autocatalyst ceased, instead, an active autocatalytic reaction started, with the result that the temperature rose acceleratedly until the final
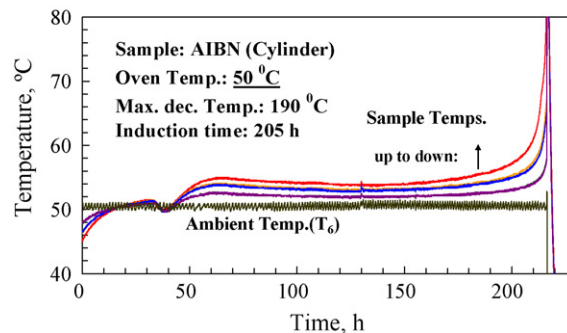
occurrence of the runaway. It was apparent that the physical state change was accompanied with the chemical reaction, and temperature distribution was very large at different position in the vessel (up to 2 K over its induction time) in the whole process. The temperature at the bottom attained to 56 °C during the induction time. It implies that AIBN behaved as quasi-autocatalysis decomposition in the container. Heat generation from its reaction was used not only to balance the heat loss through the vessel, but also the heat absorption by its physical phase transition. The decomposition took place in solid–liquid co-existing state sililar to the half-melted shaved ice.

Whereas a spherical Dewar vessel has better adiathermancy whose heat transfer coefficient is 1/8 of that of the cylinder Dewar. The critical temperature for runaway of AIBN was 45 °C. This temperature jumped ahead of the point of sublimation or melting of AIBN. After being warmed up to the surrounding temperature, the rate of heat generation of AIBN exceeded the rate of heat transfer to the surrounding throughout the whole self-heating process, with the result that the temperature of the chemical continued to increase linearly during the induction time and acceleratedly at the end until the ultimate runaway happened. There was no sign for phase change. There was no any physical state change to interfere the reaction occurrence and hence its unitary decomposition took place in the solid phase. The temperatures were very uniform throughout the vessel because of the high adiathermancy of the sphere vessel. In this case it is a typical TD type of decomposition, however it is completely different from the TD decomposition happening in the liquid phase in the DSC.
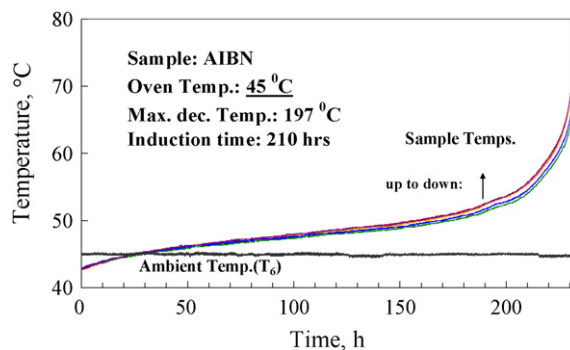

Fig. 10. Temperature profile of AIBN in the 1000 ml sphere Dewar.

It seems that the physical endothermic effect somehow inhibite the reaction, as indicated in Fig. 9. However it can never be said that the system is less dangerous. On the one hand, the reaction was continued by its autocatalysis regardless of the physical interference. On the other hand, the onset reaction may readily detour the physical effect range in case of a worse heat transfer system, as the result in Fig. 10. Therefore only after all factors that influence the self-heating are made clear, what will happen near the SADT of AIBN or other azo compounds may be clarified.

4. Conclusion

The thermal decomposition of AIBN is complicated and behaves diversely at different conditions. The intrinsic reason is that sublimation or physical phase transition stays in the area when its reaction starts. Endothermic and exothermic effects compete with each other in this area and lead to different observations. Results can depend on various factors: temperature, sample size and the conditions applied in the apparatus utilized in the experimental tests. These directly influence the self-heating behavior of AIBN near the SADT.

Non-isothermal measurement is used widely because of its time saving. However when dealing with the storage temperature as near the SADT, it may give inaccurate basic information for further calculation of kinetic and prediction of the SADT. In contrast, isothermal or lower heating rate condition may provide more closed information on the characteristics of AIBN or other azo analogue near the SADT.

Various possibilities of the decomposition of AIBN may take place in thermal analysis calorimeters: (1) the endothermic peak appears prior to its major thermal decomposition at higher heating rate, and hence the decomposition happens in liquid or gas phase; or (2) the endothermic effect is wedged to the decomposition of AIBN to form two saddled exothermic peaks at lower heating rate or isothermal conditions, and the decomposition is more likely occur at in liquid–solid phase. In the storage test, it undergoes two different types of self-heating behaviors: quasi-autocatalysis and thermal decomposition. The reaction may occur in solid, liquid, their co-existing, even gas phase.

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