Study on Thermal Decomposition Characteristics of AIBN

Xin-Rui Li*, Xin-Long Wang** and Hiroshi Koseki*
(*National Research Institute of Fire and Disaster, Japan
** Nanjing University of Science and Technology, China)
Why is AIBN studied?

- Wide application blowing agent and initiator.
- Danger: azo compound, (2,2’-Azobis (isobutyronitrile))
  - Class 5,
  - self reactive material, cautious to runaway due to self heating during storage and transportation.

Ambiguity on its thermal decomposition

1. \[ \frac{d\alpha}{dt} = k (1-\alpha)^N \] N-order reaction (TD)
2. \[ \frac{d\alpha}{dt} = k \alpha^{1-x} (1-\alpha)^{1-y} \] autocatalytic (AC)
3. Physical transformation

- basically considered as TD (thermal decomposition) type
- contradictory information came from different measurements and as a consequence led to misleading description of the overall decomposition process.
To get a comprehensive understanding, this paper

• compared the phenomena related to the thermal decomposition of AIBN in various apparatuses.

• clarified the reason causing different results, especially the phenomenon near its SADT (self accelerating decomposition temperature), a critical onset temperature of thermal explosion.
### Experimental

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Cell</th>
<th>Sample</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC8230 (Rigaku)</td>
<td>Al cell sealed</td>
<td>2-5 mg</td>
<td>at 0.5, 2, 2.5, 5, 10 and 20 K/min</td>
</tr>
<tr>
<td>TG-DTA (Rigaku)</td>
<td>Al cell open</td>
<td>2-5 mg</td>
<td>at 0.5, 2, 2.5, 5, 10 and 20 K/min</td>
</tr>
<tr>
<td>HPDSC(^{(1)}) (Mettler Toledo)</td>
<td>Al cell in N(_2)</td>
<td>10 mg</td>
<td>at 10 K/min</td>
</tr>
<tr>
<td>C80 (Setaram)</td>
<td>SUS cell sealed</td>
<td>0.5 g (^{(2)})</td>
<td>at 0.01,0.1 K/min, isothermal: 57,59,62,64 °C</td>
</tr>
<tr>
<td>Dewar vessel (^{(3)}) (UN H4)</td>
<td>500 ml, cylinder</td>
<td>260 g</td>
<td>45, 50 °C</td>
</tr>
<tr>
<td>Dewar vessel (^{(3)})</td>
<td>1000 ml, sphere</td>
<td>490 g</td>
<td>40, 45 °C</td>
</tr>
</tbody>
</table>

(1) HPDSC: High pressure DSC;  
(2) Besides AIBN, its solution in acetone (20%) and in toluene (4%) were measured;  
(3) Based on the BAM test (UN H4).
RESULTS & DISCUSSION
(1) General interpretation

(thermal decomposition) type materia

110 °C.

HPDSC, 10K/min
in N₂

DSC, 10K/min
in air

crystal state conversion
70-80 °C

melting, 102-105 °C
(2) Characteristics of AIBN near the SADT
✓ How does the physical effect interfere reaction?
✓ What is the intrinsic chemical characteristics?
How does the physical effect interfere reaction?

- Thermal decomposition analysis of AIBN by DSC
• Thermal decomposition analysis of AIBN by TG-DTA
(1) When heating rate lowers down, $T_{\text{onset}}$ of the chemical reaction shifts to lower range and endothermic peak weakens.

(2) In sealed DSC and open HPDSC, a small endothermic peak appears at low temperature, 75°C; The peak does not appear in open TG-DTA. This may be owing to the sublimation of AIBN or change of crystal.

(3) Classification of self-reactive chemicals based on TG-DTA (open) is unreasonable since evaporation or sublimation may affect the results.
What is the intrinsic chemical characteristics?
• Thermal decomposition analysis of AIBN by C80 Ramp measurement- one or two-step?
(1) In solutions, decomposition of AIBN takes place at lower temperature, and the heat generation is more than AIBN. The reason is that AIBN melting absorbs part of the heat of reaction in AIBN only.

(2) In acetone, AIBN showed two step decomposition; whereas in toluene, AIBN showed one step decomposition. Because of the volatility of acetone, AIBN was separated from solvent again.

(3) Intrinsic ("pure") chemical reaction of AIBN is one step decomposition.
• Thermal decomposition analysis of AIBN by C80

Ea determination -
\[ \ln\left(\frac{q_m}{D_0}\right) \text{ vs. } \frac{1}{RT} \]

Isothermal measurement - pseudo autocatalysis?

Same \( E_a \) – two peaks in same mechanism
• The onset temperature of the chemical reaction of AIBN shifts dependent upon its working condition.
• Physical state change of AIBN just happens in the area of its initial reaction.
• Competence between the exothermic and endothermic effects leads to various possibilities:
  — two peaks of thermal decomposition,
  — or the first peak of reaction in AIBN being not observed,
  — or sometimes instead, a small endothermic peak appearing in this area.
Behaviors of AIBN in Dewar vessels

at the early stage of a reaction during its storage and the process developing into a runaway reaction.
Plug or Lid Thermocouple
Protective tube
Dewar vessel

Sample Surface

Figure 1

U = 1.45, ~25 kg package

Overall heat transfer coefficient

Worse heat transfer condition,
1/8U ~ 200 kg package
AIBN in the 500 ml cylinder Dewar

Sample: AIBN (Cylinder)
Oven Temp.: 50 °C
Max. dec. Temp.: 190 °C
Induction time: 205 hrs

Sample Temps.
up to down:

Ambient Temp. \((T_\theta)\)

-quasi autocatalysis (AC) Type
-In solid-liquid mixing state
AIBN in the 1000 ml sphere Dewar

Sample: AIBN
Oven Temp.: 45°C
Max. dec. Temp.: 197°C
Induction time: 210 hrs

Ambient Temp. ($T_6$)

Sample Temps.

Time, h

-autocatalysis (AC) Type
-In solid state
CONCLUSIONS

- The thermal decomposition of AIBN is complicated and behaves differently in different conditions.

- The intrinsic reason is that sublimation or other physical state change lies in the area when its reaction starts. Endothermic and exothermic effects compete with each other in this area and lead to different observances.

- Results can depend on various factors: temperature, sample size, and the conditions applied in the apparatus utilized in the experimental tests.
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 their SADTs.