Effect of impurities on thermal hazard of dimethyl 2,2'-azobis(2-methylpropionate) (AIBME) in industrial application

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Abstract: Dimethyl 2,2'-azobis(2-methylpropionate) (AIBME) is an azo initiator. The substance is unstable and easily decomposes after being heated. AIBME is inevitably in contact with impurities such as acids and alkalis in the process of initiating the reaction. Some impurities may change the thermal decomposition behavior of AIBME. Therefore, in this paper, the effects of common impurities (hydrochloric acid, sodium hydroxide, iron oxide) on the thermal stability of AIBME were studied by differential scanning calorimetry (DSC). The activation energy was determined by Kissinger method and compared with pure materials. The results showed that three impurities reduced the heat release of AIBME during the decomposition process. However, hydrochloric acid reduced the activation energy of AIBME, increasing the risk of AIBME, while sodium hydroxide was the opposite. So it is necessary to avoid contact between AIBME and hydrochloric acid in industrial production.

Keywords: dimethyl 2,2'-azobis(2-methylpropionate) (AIBME), impurity, thermal stability, differential scanning calorimetry (DSC).

1 Introduction

Azo compounds are one of the commonly used initiators. During the reaction, substances such as acid and alkali are often added to catalyze reaction. When the azo compound is contacted with an incompatible substance such as an acid or alkali, the exothermic decomposition process changes, which may cause thermal runaway. Liu et al. evaluated four typical azos (azodiisobutyronitrile (AIBN), 2,2'-Azobis-(2-methylbutyronitrile) (AMBN), 2,2'-Azobisisoheptonitrile (ABVN) and dimethyl 2,2'-azobis(2-methylpropionate) (AIBME)) using DSC, TAM III and VSP2 thermal thermal techniques. The results were then analyzed using a nonlinear optimization model and thermal runaway of ABVN was studied under acid and alkali conditions [1.2]. At present, most of the research on azo initiators is concentrated on pure substances, and the influence of impurities on its thermal decomposition characteristics is still rarely. Therefore, it is necessary to study the incompatible materials for

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azo initiators, so as to provide a theoretical reference for practical applications. AIBME is more thermally sensitive. In the production process, AIBME is inevitably in contact with acids, alkalis and other impurities, which may affect the thermal decomposition of AIBME. In order to investigate the thermal decomposition characteristics of AIBME during using, this paper studied the effects of several common impurities (hydrochloric acid (HCl), sodium hydroxide (NaOH) and ferric oxide (Fe_2O_3)) on the thermal decomposition of AIBME. In this paper, a differential scanning calorimeter (DSC) was used to test AIBME mixed with hydrochloric acid solution, sodium hydroxide solution and ferric oxide powder at different heating rates (β), and the heat flow curves were obtained to provide data foundation for kinetic calculation. The Kissinger method was used to calculate the activation energy (E) of AIBME mixed with different impurities, which provided a theoretical reference for industrial applications.

2 Experimental

2.1 Differential Scanning Calorimeter (DSC)

The thermal decomposition of the material was experimentally analyzed using a differential scanning calorimeter (DSC) manufactured by METTLER. In the experiment, the test cell was made of gold-plated high-pressure helium, and nitrogen was used as a protective gas.

2.2 Materials

AIBME with a purity of 98% was used in this study. It was used as-obtained without further purification. HCl and NaOH solution with a concentration of 6 mol·L^{-1} and Fe_2O_3 with a purity of 98% were used as additives. The total mass of the sample is about 4 mg, and the ratio of AIBME to impurities is 3:1. The heating rate selected for temperature-programmed ramp was 1, 2, 5 and 10 ℃ /min. The thermal analyses were investigated from 30 to 200 ℃.

2.3 Reaction kinetic calculation method

Kissinger method was used to calculate activation energy. After the differential deformation of the formula $\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n$, the following formula is obtained:

$$\ln\left(\frac{\beta_i}{T_{Pi}^2}\right) = \ln\left(\frac{A_K R}{E_K}\right) - \frac{E_K}{RT_{pi}} \quad (1)$$

Activation energy can be obtained through the linear plot of $\ln\left(\frac{\beta_i}{T_{Pi}^2}\right)$ versus $\frac{1}{T_{pi}}$.

3 Results and discussion

3.1 AIBME thermal decomposition mixed with HCl solution, NaOH solution and Fe_2O_3

The AIBME was mixed with HCl and NaOH solution having a concentration of 6 mol·L^{-1} and Fe_2O_3 with a purity of 98%. The mixtures were subjected to DSC experiments at the heating rates of 1 °C·min^{-1}, 2 °C·min^{-1}, 5 °C·min^{-1}, and 10 °C·min^{-1} to obtain the heat flow curves under the corresponding conditions. The heat flow curves are shown in Figure 1-3. The relevant thermodynamic parameters such as initial decomposition temperature (T_{onset}), decomposition peak temperature (T_{pi}) and heat release (Q) are listed in Table 1-3. Compared with pure AIBME [3], AIBME mixed with HCl solution, NaOH solution and Fe_2O_3 had little change in initial decomposition temperature and decomposition peak temperature. And no obvious change in reaction mode. But the average heat release was changed from 863.40 J/g to 653.31 J/g,824.70 J/g and 809.55 J/g, respectively. It showed that incompatible substance, especially HCl, could decreased the heat release of AIBME.

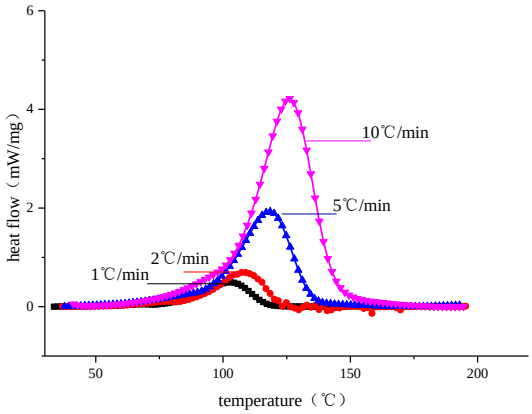

Figure 1 DSC heat flow curves of AIBME mixed with HCl solution at different heating rates

Table 1 Thermal decomposition parameters of AIBME mixed with HCl solution

β(℃/min)	T_{onset} (℃)	T_{pi} (℃)	Q (J/g)
1	82.27	102.74	726.90
2	105.89	107.09	531.72
5	94.45	118.31	635.52
10	102.30	126.50	719.11

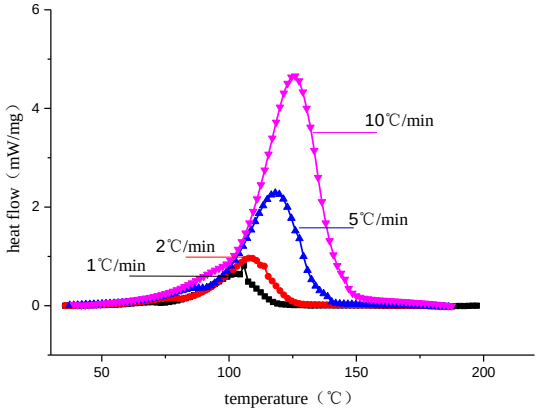

Figure 2 DSC heat flow curves of AIBME mixed with NaOH solution at different heating rates

Table 2 Thermal decomposition parameters of AIBME mixed with NaOH solution

β(℃ /min)	T_{onset} (℃)	T_{pi} (℃)	Q (J/g)
1	78.33	105.96	929.74
2	79.95	108.72	764.71
5	94.58	118.55	787.08
10	101.67	125.96	817.27

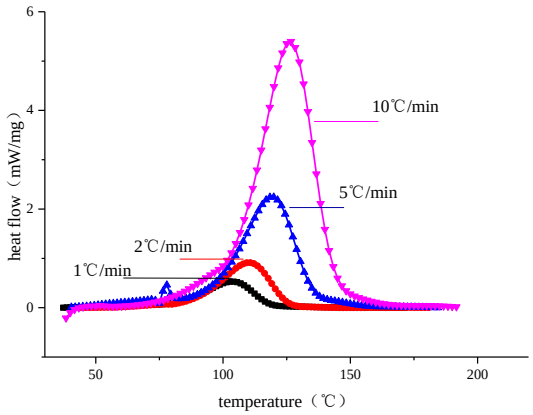

Figure 3 DSC heat flow curves of AIBME mixed with Fe_2O_3 at different heating rates

Table 3 Thermal decomposition parameters of AIBME mixed with Fe_2O_3

β(℃ /min)	T_{onset} (℃)	T_{pi} (℃)	Q (J/g)
1	81.75	103.70	852.10
2	87.97	110.28	684.95
5	95.50	119.44	785.68
10	102.85	126.94	915.48

3.2 Kinetic calculation

DSC data was processed using the Kissinger method, as shown in Figure 4 . Activation energy can be calculated through the slope of the linear plot of $\ln\left(\frac{\beta_i}{T_{Pi}^2}\right)$ versus $\frac{1}{T_{pi}}$. Slope under three conditions were obtained by linear fitting of experimental data. *E* of AIBME mixed with HCl solution, NaOH solution and Fe_2O_3 is 107.73KJ·mol^{-1}, 136.19KJ·mol^{-1}, 117.26KJ·mol^{-1}, respectively. Compared with pure AIBME [3], AIBME mixed with HCl solution has a lower activation energy, AIBME mixed with NaOH solution, and the activation energy of AIBME mixed with Fe_2O_3 has little changed. That is, HCl solution promotes the decomposition of AIBME and NaOH solution has the opposite effect.

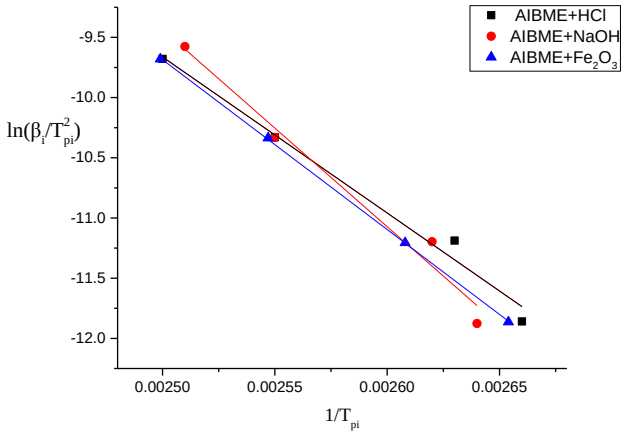

Figure 4 The activation energy of AIBME obtained by Kissinger method

4 Conclusion

The thermal decomposition tests were used to study the thermal decomposition characteristics of AIBME mixed with different incompatible materials. When AIBME was mixed with different incompatible materials, the heat release was reduced, and the mixing with HCl solution was the largest. However, the HCl solution reduced the activation energy of AIBME while reducing the heat. NaOH solution increaseD the activation energy of AIBME. Ferric oxide had little effect on AIBME thermal decomposition. After the addition of impurities, the decomposition process of AIBME did not change significantly.

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6 Reference

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