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Kinetic analysis and self-accelerating decomposition temperature (SADT) of β-nitroso-α-naphthol

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ABSTRACT

To study the thermal hazard of β-nitroso-α-naphthol, both dynamic and isothermal tests were performed with a differential scanning calorimeter (DSC). The dynamic tests indicated that the initial decomposition temperature of β-nitroso-α-naphthol ranged from 153 °C to 173 °C. The interrupt-rescanning method verified the autocatalytic characteristic of β-nitroso-α-naphthol decomposition. DSC curves obtained at five constant temperatures confirmed that the decomposition of β-nitroso-α-naphthol was an autocatalytic reaction. Activation energy E was $149 \pm 8\,kJ\,mol^{-1}$ calculated by Kissinger method. E values calculated by induction period method and isothermal method were in line with that obtained by Friedman method. On the basis of the kinetic analysis, the safety parameter SADT of β-nitroso-α-naphthol in 50 kg standard packaging was 81 °C based on Semenov model and 67 °C based on Frank-Kamenetskii model.
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1. Introduction

β-Nitroso-α-naphthol, widely used for determining the content of cobalt, zirconium, copper, uranium, iron, ruthenium and palladium, can also be used in organic synthesis. In recent years, investigations of β-nitroso-α-naphthol have mainly focused on the elemental detection and organic synthesis (Lemos et al., 2007; Lemos and Gama, 2010; Cheng, 1954; Minagawa et al., 2001; Ghosh et al., 1981; Manning and Menis, 1962). In fact, due to the presence of the nitroso group, β-nitroso-α-naphthol has poor thermal stability. However, its thermal hazard has not been paid enough attention and few studies thereof have been reported. In this paper, in order to study the thermal behaviors of β-nitroso-α-naphthol, dynamic and isothermal tests were carried out by DSC. The results showed that its decomposition had an autocatalytic mode. Autocatalytic decomposition is considered hazardous because it gives rise to sudden heat evolution, and is often initiated with unexpected external influences. Therefore, it is necessary to perform further researches in this regard. Kinetic parameters (activation energy E, and pre-exponential factor A) of β-nitroso-α-naphthol were obtained by isothermal induction period method, Kissinger method (Kissinger, 1956), Friedman method (Friedman, 1964) and an isothermal method, and its self-accelerating decomposition temperature (SADT) was predicted by employing Semenov model (Yu and Hasegawa, 1996; Sun et al., 2001) and Frank-Kamenetskii model (Sun and Ding, China), which would contribute to the safe handling of β-nitroso-α-naphthol and the optimization of its production process.

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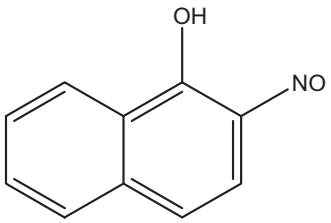

Fig. 1 – Structural formula of β-nitroso-α-naphthol.

Table 1 – Dynamic DSC test conditions.

Heating rate (°C min^{-1})	Sample mass (mg)	Temperature range (°C)
1	2.00	140–165
2	2.00	140–180
4	2.01	140–190
8	1.99	140–200
10	2.00	140–210

2. Material and methods

2.1. *Reagent*

The reagent used was β-nitroso-α-naphthol of 98 mass%, as a yellow powder, purchased from Aladdin Reagents Company. Its structural formula is shown in Fig. 1.

2.2. *Methods and conditions*

All the tests were performed by a heat flux differential scanning calorimeter (DSC-1) with sensitivity of ±0.04 μW, manufactured by METTLER TOLEDO Corp., Switzerland. The samples were sealed in high pressure steel crucibles (type of ME-51140404) with gold-plated pads, which can bear a pressure of 15 MPa. A same empty crucible was used as a reference. The crucibles were sealed under air atmosphere. All the tests in dynamic and isothermal modes were performed under dry nitrogen with a flow rate of 80 mL min^{-1}. The detailed experimental conditions are shown in Tables 1 and 2.

3. Results and discussion

3.1. *Thermal behaviors under dynamic condition*

The heat flow and the change in the reaction rate with temperature at different heating rates are illustrated in Fig. 2. The corresponding characteristic parameters are given in Table 3.

It can be seen from Fig. 2 that there is one exothermic peak on each of the DSC curves. The initial decomposition temperature of β-nitroso-α-naphthol ranged from 153 °C to 173 °C. From Table 3, the average specific decomposition heat of the reaction was 647 J g^{-1}, according to assessment criteria for the severity of a runaway reaction (Stoessel, 2008), it occupies critical level.

Table 2 – Isothermal DSC test conditions.

Temperature (°C)	Sample mass (mg)	Time (h)
132	2.01	2
134	2.00	1.8
136	2.01	1.8
138	2.00	1.8
140	2.01	1.8

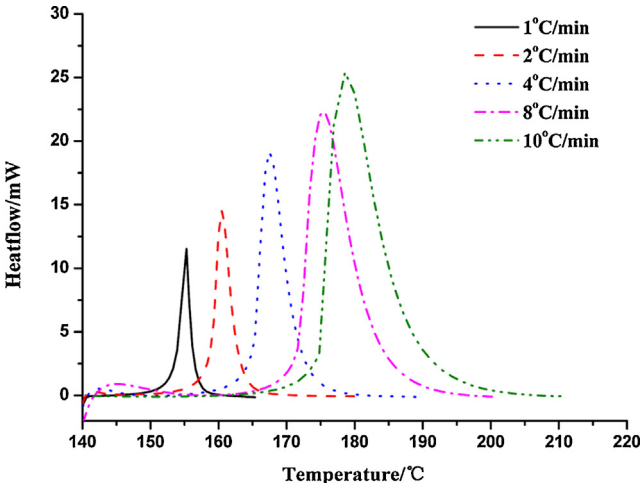

Fig. 2 – Heat flow of β-nitroso-α-naphthol under different heating rates.

Table 3 – Characteristic parameters of β-nitroso-α-naphthol obtained by dynamic DSC tests.

Heating rate (°C min^{-1})	T_{onset} (°C)	T_{peak} (°C)	ΔH (J g^{-1})
1	153	155	640
2	158	160	666
4	154	167	668
8	171	176	629
10	173	179	631

3.2. *Verification of autocatalytic reaction*

Generally, the curves of the autocatalytic reaction in a dynamic mode are characterized by such features as narrow peaks, high maximum heat release rates and high energy potentials (Stoessel, 2008). From Fig. 2, the decomposition of β-nitroso-α-naphthol seems to be autocatalytic.

To further verify that the thermal decomposition reaction of β-nitroso-α-naphthol is an autocatalytic reaction, another rapid identification method, i.e., an interrupt-rescanning method (Roduit et al., 2013; Yang et al., 2014) briefly shown in Fig. 3 was used. In the interrupt-rescanning method, firstly, a dynamic scanning test was performed on the samples to obtain the initial decomposition temperature, peak temperature and heat. Then the same sample with similar mass was heated from the initial temperature T_1 to the intermediate temperature T (the interrupt temperature) using the same

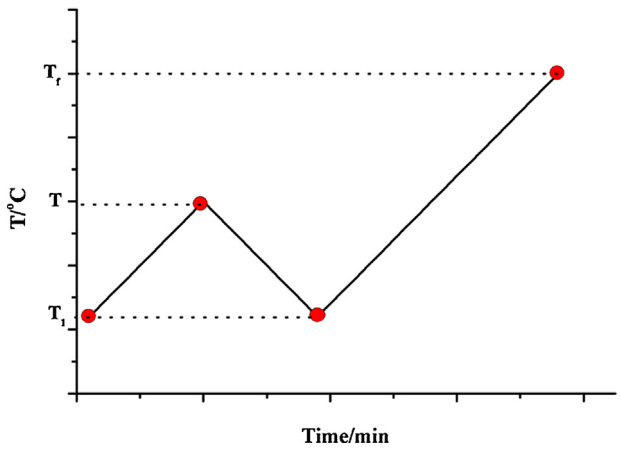

Fig. 3 – Schematic diagram of interrupt reactions.

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