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Thermal hazards and kinetic analysis of salicyl hydroxamic acid under isothermal and adiabatic conditions

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ABSTRACT

Kinetic study and thermal hazards analysis on the thermal decomposition of salicyl hydroxamic acid (SHA) was carried out using differential scanning calorimetry (DSC). The isothermal and dynamic differential scanning calorimetric curves were recorded, respectively. The temperature dependence of the observed induction periods suggests an autocatalytic decomposition mechanism, which was supported by the conversion-reduced time plots. The differential and integral isoconversional methods were used to obtain the kinetic parameters. The decomposition mechanism model of the first peak was $f(\alpha)=\alpha^{1.49}(1-\alpha)^{1.59}$. Moreover, the isothermal temperature induction period were studied to obtain the activation energy, which was close to that obtained by the isoconversional integral method. The adiabatic accelerating calorimetry (ARC) was also employed to evaluate the thermal hazards. The adiabatic activation parameters were also obtained based on the autocatalytic reaction model.

1. Introduction

Salicylhydroxamic acid (SHA) is mainly used as a collector for rare earth, copper oxide, lead and zinc oxide, gold, kaolin ores and so on. It can also be used as extraction solvent and organic synthesis intermediates. Many hydroxamic acids have a strong metal ion chelating activity [1], which makes SHA an important class of metal-complexing agent [2,3]. Since hydroxamic acids are weak proton donors, it can also be applied in other areas such as enzyme inhibitors, iron carrier protein, DNA cutting, metal nucleic acid enzymes, drug delivery system [4–6]. Typically the hydroxamic acid exists in two forms, like, keto or enol, i.e., hydroxamic acids and hydroxamic acid coexist, which can be considered as the same material. The spectral data showed that enol is the main existence form [7]. The hydroxamic acid has properties of both amide and oxime group. However, the oxime group is a reactive organic functional group, which makes it possible to decompose under thermal excitation or something like that.

There are lots of investigations of hydroxamic acid, involving synthetic process [8,9], its contribution to the beneficiation as a collecting agent [10,11], its biodegradable characteristics [12,13] and its functions as enzyme inhibitor [14]. Moreover, Proskurnin etc.et al. [15] used thermal-lens spectrometry to determine the SHA in the aqueous solution of ferric iron. Liu et al. [9] used salicylic acid and hydroxylamine as raw materials to synthesize salicylhydroxamic acid, and characterized it by IR. Bhaduri [16] used SHA as an analytical reagent of uranium, vanadium, molybdenum and iron. Nevertheless, the study on thermal decomposition of SHA is rare. Wendlandt and Hoiberg [17] employed differential thermal analysis (DTA) to "finger-print" SHA, and provided its thermal weight-loss data by thermogravimetric analysis (TGA).

The purpose of this paper is to study the thermal behavior of SHA under different temperature control modes. The results showed decomposition occurs in solid under isothermal conditions. However, under dynamic conditions, SHA can decompose in solid or liquid. Analysis of DSC test results in isothermal mode showed that the decomposition followed a complex autocatalytic mechanism. Chemical compounds able to decompose autocatalytically are considered more hazardous because the decomposition reactions can accelerate even under isothermal conditions during prolonged storage [18]. Furthermore, ARC test was carried out to evaluate its thermal risk, and the kinetic parameters under adiabatic conditions were also obtained. This research is helpful for the safe handling of SHA and the optimization of the process.

2. Experimental

DSC, which has been employed broadly for evaluating thermal hazards [19] in various industries, is easy to operate, gives quantitative results, and provides information on sensitivity (exothermic

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Table 1
ARC test conditions.

Sample	Bomb mass (g)	$C_{p,b}$ (J g^{-1} K^{-1})	Sample mass (g)	$C_{p,s}$ (J g^{-1} K^{-1})	Phi-factor	Temperature range (°C)
SHA	14.477	0.42	0.226	2	14.5	100–225

Note: $C_{p,b}$ and $C_{p,s}$ are specific heat capacity of bomb and sample, the value of the latter is estimated.

onset temperature, T_0) and severity (heat of decomposition, ΔH) at the same time. DSC is regarded as a useful tool for the evaluation of thermal hazards and for the investigation of decomposition mechanisms of reactive chemicals if the experiments are carried out carefully.

All DSC tests were carried out using a heat flux DSC manufactured by Switzerland METTLER TOLEDO. The calorimeter was calibrated with indium and zinc for temperature and heatflow. High pressure steel crucibles with gold-plated pads were used for all experiments and an 80 mL min^{-1} N_2 purge gas was applied. The thermal behavior of compound in non-isothermal mode was followed at heating rates of 1, 2, 4, 8 and 10 K min^{-1}. The results from non-isothermal analysis were used to set out the temperature range of isothermal tests. The isothermal decomposition reaction was followed up starting from several temperatures lower than the melting point. SHA was of reagent grade (Aladdin) with masses about 1.5 mg.

ARC [20] can simulate the potential runaway reaction under adiabatic condition and quantify its temperature and pressure hazards. Thermodynamics and kinetics can be calculated with relative theory basing on test data. Adiabatic initial decomposition temperature T_0, self-heating rate, time to maximum rate and other parameters can be obtained to evaluate the thermal stability or thermal hazards.

The ES-ARC from British THT was employed, the operating mode is "Heat–Wait–Seek (HWS)", the heating gradient is 5 °C, the waiting time is 10 min, and the detection sensitivity is 0.02 °C min^{-1}. The type of test sell is HC-MBQ. The conditions of sample and bomb are shown in Table 1.

3. Results and discussion

3.1. DSC test

3.1.1. Non-isothermal decomposition characteristics

A typical run for SHA at different heating rates is shown in Fig. 1. When heated with constant rates SHA decomposes suddenly after melting when the heating rate is larger than 4 °C min^{-1}. The result was consistent with that in Ref. [17], in which the coupling of heat absorption and generation was founded at 5 °C min^{-1}. It's due to the competition of exothermic decomposition and endothermic melting. At low heating rates, the melting is very weak relative to decomposition, so only exothermic signal is detected. Under high heating rates, the decomposition at initial stage is weak compared with melting, so it shows absorption of heat apparently, but as time goes on, the exothermic decomposition gradually strengthens so that it exceeds the melting heatflow, resulting in exothermic signal. The characteristic parameters are given in Table 2.

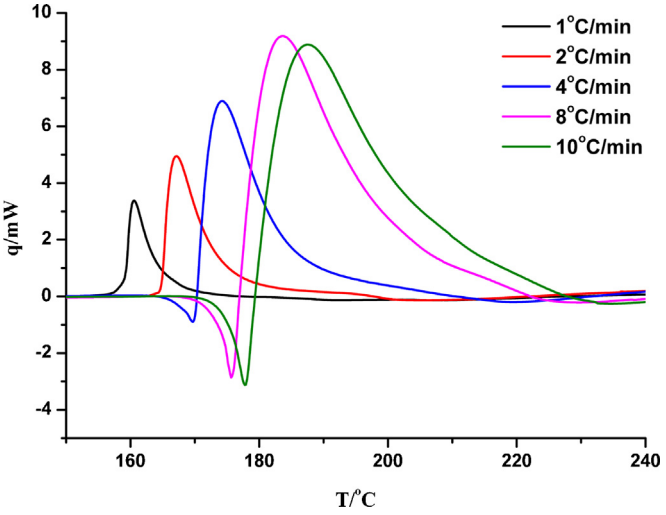

Fig. 1. Heat flow traces of SHA recorded by DSC at different heating rates.

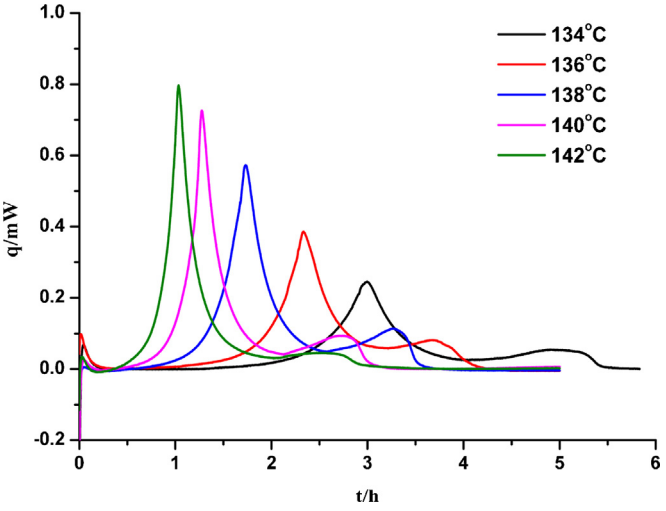

Fig. 2. Isothermal DSC curves of SHA at different temperatures.

3.1.2. Isothermal decomposition characteristics

On the basis of dynamic DSC tests, several experiments in isothermal regime were performed at 134 °C, 136 °C, 138 °C, 140 °C, 142 °C to study the thermal behavior in solid state. The DSC curves are shown in Fig. 2. It can be observed that an exothermal peak appeared after a characteristic temperature-dependent induction

Table 2
Characteristic parameters of SHA obtained by dynamic DSC tests.

Heating rate (°C min^{-1})	T_{min} (°C)	T_{max} (°C)	ΔH (J g^{-1})	Average ΔH (J g^{-1})
1	–	160.6	701.3	801.8
2	–	167.1	766.0	
4	169.7	174.2	885.5	
8	175.7	183.6	872.4	
10	177.8	187.6	784.0	

Note: T_{min} and T_{max} are the peak temperature of the melting and decomposition, respectively.