Research on the thermal stability of 2-amino-3,5-dichloro-N-methylbenzamide (ADMBA) applying DSC

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Abstract: To study the thermal stability of 2-amino-3,5-dichloro-N-methylbenzamide (ADMBA), five dynamic DSC curves were initially used to obtain the apparent thermodynamic data, such as the activation energy, the initial decomposition temperature, and heat release for the thermal decomposition from samples. Combined with AKTS kinetic software and the Friedman method, the simulation calculation for the DSC data was conducted to predict thermal stability, such as TMRad and SADT. The TD24 was 254.3℃ and SADT was 221℃, respectively, utilizing DSC and AKTS.

1. Introduction
Tetrachlorantraniliprole is a novel kind of insecticide commercialized by the Sinochem Group in 2014 and can be widely used in a variety of plants such as rice, corn, and vegetables.[1,2] The title compound 2-amino-3, 5-dichloro-N-methylbenzamide (ADMBA) is a crucial intermediate product for manufacturing the active ingredient SYP-9080. Still, there is little literature about the thermal safety criteria of ADMBA. In recent years, familiar cases reported in the published literature [3–8] demonstrate that the experimental data gathered in varied thermal apparatus (such as DSC and C80) with a small number of specimens can be exploited for the large scale thermal peculiarities of samples via the thermal kinetic analysis.

In this work, we present the thermal stability of ADMBA using the DSC and AKTS program. A series of thermal safety parameters such as TMRad, SADT, the activation energy, the initial decomposition temperature, and heat release for the thermal decomposition from samples were also gleaned.

2. Experimental Section
The ADMBA (98.0%, chemically pure) used in this work was obtained from the Sinochem Group (China). The DSC tests were conducted using DSC3 commercialized by Mettler Toledo. A 25μL golden container was applied and a 3-5mg sample was supplied to the crucible, and subsequently closed in the air. The DSC tests were carried out at the heating rates of 0.5, 1.0, 2.0, 4.0, 8.0℃ꞏmin -1, respectively. The kinetic analysis software from the Swiss company AKTS was utilized to attain thermal safety parameters.
3. Results and Discussion

The test results of the differential scanning calorimeter are listed in Figure 1 and Table 1. A differential scanning calorimeter (DSC3) was utilized to analyze ADMBA thermal decomposition processes of five heating rates. Figure 1 indicates that a strong exothermic peak appears between 350-425°C and the average decomposition heat reaches -852.41 J/g. The results indicate that when the heating rate $\beta$ increases, thermal hysteresis becomes more pronounced, so the initial decomposition temperature $T_o$ and exothermic peak temperature $T_{peak}$ shift to the higher temperature region. By contrast, the initial decomposition and peak temperatures both shift to the lower temperature area.

![Fig. 1 Five heat flow curves of ADMBA tested using DSC](image)

| $\beta$ (°C⋅min$^{-1}$) | mass (mg) | $T_o$ (°C) | $T_{peak}$ (°C) | $\Delta H$ (J⋅g$^{-1}$) |
|-------------------------|-----------|------------|----------------|-------------------------|
| 0.5                     | 3.561     | 345.830    | 354.323        | -897.344               |
| 1.0                     | 3.472     | 359.020    | 368.512        | -868.045               |
| 2.0                     | 3.380     | 377.930    | 388.790        | -723.568               |
| 4.0                     | 4.717     | 395.707    | 407.277        | -1027.949              |
| 8.0                     | 3.157     | 401.144    | 421.061        | -745.165               |

The elaboration of the statistic information has been represented by the differential isoconversional method interpolated by Friedman and AKTS Software. Broadly, the approach does not require a precise presumption of function $f(\alpha)$ and does not embrace the constancy of the activation energy and the pre-exponential factor in the process. The expression of decomposition rate can be gained as follows:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha)$$

After taking a logarithm on both sides, we obtain the expression as follows:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[Af(\alpha)] - \frac{E_a}{RT} \frac{1}{T}$$
In this work, (1) \( \ln(\text{da}/\text{dt})_\alpha \) vs 1000/T of five DSC curves; (2) the activation energy vs the reaction process are expressed in Figures 2 and 3, respectively.

![Fig. 2 Curves of \( \ln(\text{da}/\text{dt})_\alpha \) vs 1000/T of five DSC tests](image)

The red line (Figure 3) shows that the activation energy \( E \) differs from 120 to 140 kJ/mol, not a constant, which implies that the decomposition of ADMBA is comparatively convoluted. The calculation of the kinetic parameters \( E \) and \( A \) of the decomposition described in Figure 3 allowed for the reaction course's simulation at comparison and distinct heating rates of the acquired DSC information. The relevant comparison of the two types of curves is exhibited in Figure 4.
Fig. 4 Two types curves of tested (color lines) and simulated course (black lines)

TD_{24} is a key parameter to evaluate the thermal safety of chemicals. The TD_{24} was simulated via AKTS Software utilizing calculated parameters from DSC which were given in Fig 5. The TMR_{ad} = 24 values for ADMBA amount to 254.3°C.

Fig. 5 Curves of Thermal Runaway Time vs Temperature in adiabatic condition

Another key criterion is named SADT (self-accelerating decomposition temperature) related to the field of thermal safety, packaging, self-reactive chemicals, and transport. There are four test methods to obtain SADT advised by the U.N. agency, while most of them need a considerable number of test samples and a long period. In this job, the mg-level DSC tests can be used to predict the SADT for the 50kg package, avoiding expensive and time-consuming kg-level experiments for calorimetric tests. As shown in Figure 6, the simulated SADT appeared to be 221°C from the measurable results of differential scanning calorimeter.
4. Conclusions
To study the thermal stability of 2-amino-3,5-dichloro-N-methylbenzamide (ADMBA), five sets of DSC curves were initially used to obtain the apparent thermodynamic data: (1) the activation energy $E$ is from 120 to 140 kJ/mol, not a constant; (2) the initial decomposition temperature varies from 345°C to 402°C; (3) the measured average heat release for the thermal decomposition of ADMBA is -852.41 J/g; (4) combined with AKTS kinetic software and the Friedman method, the simulation calculation for the DSC data was conducted to predict thermal stability. The $TD_{24}$ was 254.3°C and SADT was 221°C, respectively. The acquisition of all the apparent safety parameters is crucial to evaluate the thermal stability of ADMBA. This not only provides more accurate design parameters, but also improves design compliance, effectively controls risk, reduces investment, and reduces consumption in the future.

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