# Study on kinetics, thermodynamics, and thermal hazards of the synthesis of clethodim based on a fatal accident

Jianna Wang*[a,b], Hongyuan Wei[a] , Lin Hao[a], Mengmeng Han[b], Xiaohui Jin[b] , Tiantian Zeng[b], Haiyan Guo[b], Yanxia Ning[b].

[a] *School of Chemical Engineering, Tianjin University, Tianjin 300350, China;*

[b] *Shandong Rainbow Process Safety CO., Ltd. Jinan Shandong 250000, China;*

**Corresponding author email: wangjn@rainbowagro.com*

**Keywords:** Clethodim, *O*-(3-chloro-2-propyl) hydroxylamine, thermodynamic, kinetic, thermal hazard.

## Extended Abstract

On February 11, 2020, a serious explosion occurred in the clethodim production workshop of an agrochemical company in Liaoning, China, resulting in 5 deaths and 10 injuries. This was a typical explosion accident caused by loss control of reaction. Similar accident happened in India at UPL's Jhagadia plant in Gujarat, on February 23, 2021. This article conducted thermodynamic and kinetic tests on the chemicals and reactions involved in the accident, simulated the operating conditions during the accident, and combined all the above test results to evaluate the criticality of reaction hazards.

The target reaction was condensation of *O*-(3-chloro-2-propyl) hydroxylamine (CPHA) and 5-[2-(Ethylthio)-propyl]-3-hydroxy-2-propionyl-2-cyclohexen-1-one (EPCO) to produce clethodim with petroleum ether as the solvent. Tests results showed that CPHA and clethodim decomposed intensely under heat, which was the main reason for the serious explosion, and the mischarge of CPHA and EPCO together to CPHA tank was the reason to induce the decomposition of CPHA and clethodim. DSC (Fig. 1) tests showed that the initial decomposition temperature ($T_{left}$) of CPHA was 80-120℃ at different heating rates, $T_{D24}$ was 60-70℃, and the decomposition heat release ($Q_d$) was about 2600-3500J/g. The decomposition rate of CPHA was fast and autocatalytic. Meanwhile, $T_{left}$, $T_{D24}$ and $Q_d$ of clethodim was 100-120℃, 70-80℃ and 1000-1500 J/g, respectively. In addition, RC1 calorimetry tests showed that heat release of condensation reaction was about 45 kJ/mol (EPCO), adiabatic temperature rise ($\Delta T_{ad}$) was 35 K. Kinetic experiments showed that it was a typical n-order reaction (Fig. 3), the total reaction order was 2. The activation energy ($E_a$) was about 51.4 kJ/mol (Fig. 2), and the pre-exponential factor (A) was $1\times10^5$, therefore its reaction rate equation can be represented as：

$$-r = 1 \cdot 10^5 \cdot e^{-\frac{51.4}{RT}} \cdot C_{CPHA} \cdot C_{EPCO}\text{。}$$

Hence, we can reasonably infer that the reaction rate of this condensation reaction more sensitive to reactant concentration compared with reaction temperature. Although the hazard criticality of normal process was level 5 ($T_p$ 50℃， MTSR 85℃, MTT 80℃，

$T_{D24}$ 75℃ ) it was still under control due to low reaction speed, good stirring, and heat transfer. However, during that accident, CPHA and EPCO were mischarged into CPHA tank in mass ratio of 3:2 without solvent. In this case, reaction rate was much faster than normal, temperature rose to above 100℃ quickly, which caused the explosion accident.

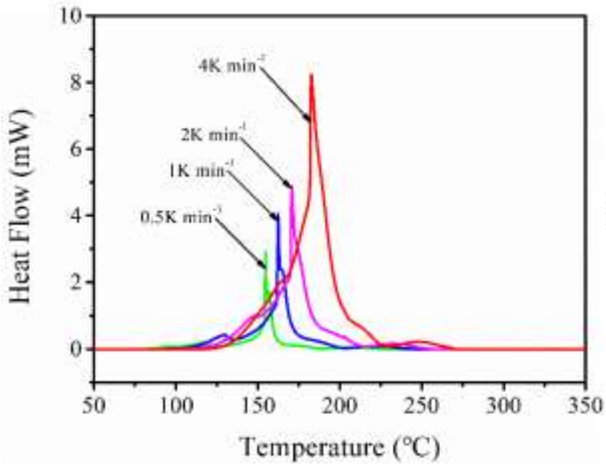



Fig.1. DSC dynamic scanning curves of CPHA at different heating rates

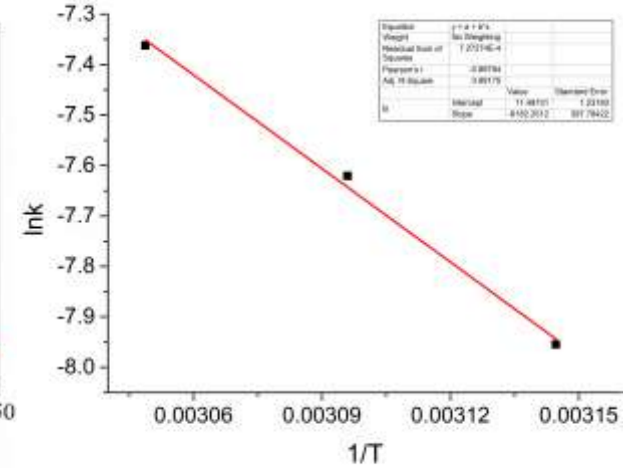
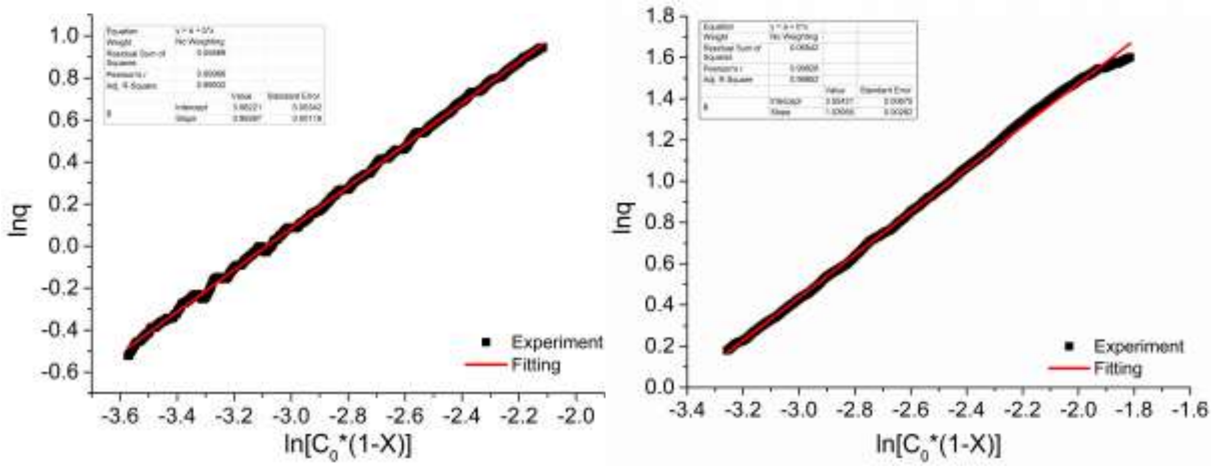



Fig 2. Fitted curve of lnk *vs*. 1/T to get $E_a$.




(a) (b)

Fig. 3（a, b） The experiment and fitting curve to get reaction order of CPHA and EPCO.