

Thermal, Kinetic and Safety Aspects of a Thermally In-Stable Reaction Mixture: Mastering the Thermal Runaway Situations

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Abstract: This article reports to the hazard evaluation studies of a laboratory scale reaction involving 1, 3-diethyl propanedioate and Fuming Nitric acid to form diethyl 2-nitropropanedioate. The process has been optimized and scheduled to the pilot scale batches after process safety evaluation. Fuming Nitric acid addition to 1,3-Diethyl propanedioate at 7°C is highly exothermic reaction with an adiabatic-temperature-rise of 113°C according for RC1e experiment. But the mixture strongly shows an exothermic event at an onset temperature of 60°C to a maximum temperature of 538°C within few seconds with a massive pressure rise in ARC experiment. Indeed, these hazard evaluation experimental results are clear to understand the hazards of the reaction in case of failing in controlled addition, which helped us to redesign the laboratory scale process and notified the required control measures at plant scale.

Keywords: Hazards evaluation, risk assessment.

1. INTRODUCTION

Reaction hazard assessment [1-7] towards process safety management is a disciplined framework for managing and integrity of controlling systems at various stages by applying good engineering, operating and maintenance practice. It deals with the prevention and control of risks that have the potential to occur incidents or accidents. Hence, it is important to study the processes in order to anticipate the risks that will occur.

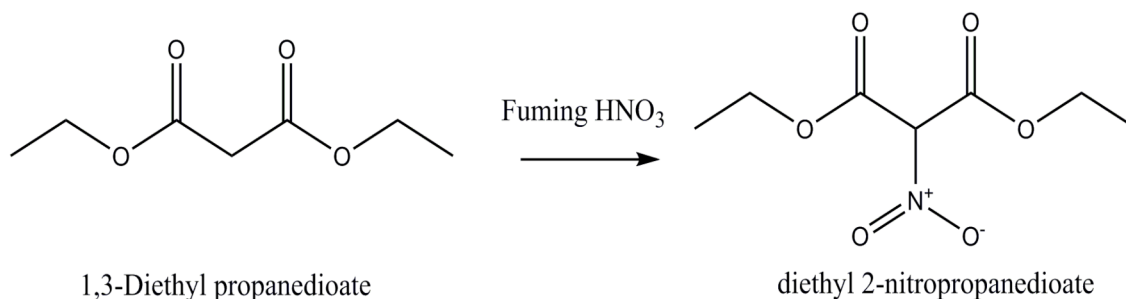
2. JUST EXOTHERMIC? OR WHETHER EXOTHERM LEADS TO RUNAWAY?

Although useful preliminary information may be obtained from thermochemical calculations and literature surveys, in most cases, some degree of experimentation will be needed to assess the hazards more accurately. Mastering the runaway [8-13] situations are always a challenge while developing the processes at laboratory scale. When assessing the chemical reactions, a distinction should be made between the reaction in safe conditions and in runaway conditions. Every exothermic reaction may not turn up to runaway situation. It need specific conditions to behave as a runaway. While assessing the hazards about exothermic reactions, only the heat of reaction and adiabatic-temperature-rise data from a reaction calorimeter may not be sufficient to conclude about

runaway possibilities. Isothermal reaction calorimeter data provide the information about the reaction how critical/severe it is and useful in designing and estimating the cooling requirement and time of addition at commercial scale operations. Hence, an adiabatic calorimeter [14-18] must be used to check the thermal stability of the reaction mixture at elevated temperatures. Most of the thermal runaway situations for the chemical reactions are due to its thermal instability of the reaction mixture, whereas the heat generation rate exceeds the heat removal rate which cause the rise in temperature and pressure of the reaction mass. If the reaction mass is unstable at a temperature which possible to influence by its reaction heat due to lack of cooling failure or uncontrolled addition of the reagent may trigger into a loss of control. Of course, there are several other reasons for a runaway situation to occur apart from the reaction hazard evaluation like accumulation of energy, self-heating, incompatibility with other materials, manual error, properties of the handling substances, failure in design, lack of knowledge on the hazards, insufficient measures, ignorance of hypothetical conditions, poor maintenance practice etc.

During our reaction hazard evaluation studies at our process safety lab for an optimised laboratory scale process (Scheme 1) which was planned to scale-up, the hazards of the reaction were identified experimentally. Thermal, kinetic and safety aspects of the process were developed in the laboratory stage, which was helped us to redesign the process.

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Scheme 1: Formation of diethyl 2-nitropropanedioate .

3. EXPERIMENTAL PROCEDURE

Mettler Toledo's Isothermal Reaction calorimeter (RC1e) and HEL's adiabatic reaction calorimeter (ARC) were used for assessing the reaction hazards. Initially we conducted the RC1e experiment for the process, i.e., 1,3-Diethyl propanedioate (250 g) was cooled to 7°C and added Fuming Nitric acid (343.7 g) slowly at 7°C over a period of 140 min. After addition, the reaction mass temperature was raised to 17°C and maintained isothermally for 12 hours at 7°C for the progress of the reaction.

As the reaction is highly exothermic from RC1e data, we also examined the thermal stability of 1,3-Diethyl propanedioate and Fuming Nitric acid mixture (3 g) after addition in RC1e experiment.

The following information was generated by both RC1e and ARC experimental data.

- Heat of reaction, adiabatic-temperature-rise and accumulation of reaction calorimetric data.
- Onset temperature of decomposition, maximum temperature due to decomposition, self-heat rate, pressure-rising rate of adiabatic reaction calorimetric data.
- Kinetics information.
- T_{D24} estimation.
- Criticality class index.
- How to decide the number of lots of safer design of the process.

4. RESULTS AND DISCUSSION

As per the RC1e results, the total heat of reaction for Fuming Nitric acid addition to 1,3-Diethyl propanedioate at 7°C is 113.93 kJ (Figure 1) with an

adiabatic-temperature-rise of 113°C ($\Delta T_{ad} = Q_r / M_r \cdot C_p = 113.93 / 0.593 \cdot 1.70$). The adiabatic-temperature-rise 113°C indicates that the reaction is significant exothermic. Considering as a batch reaction conditions, the maximum temperature of the synthesis reaction, i.e. MTSR ($\Delta T_{ad} + T_p = 113 + 7$) is 120°C. The boiling points of 1, 3-Diethyl propanedioate and Fuming Nitric acid are 199°C and 83°C respectively.

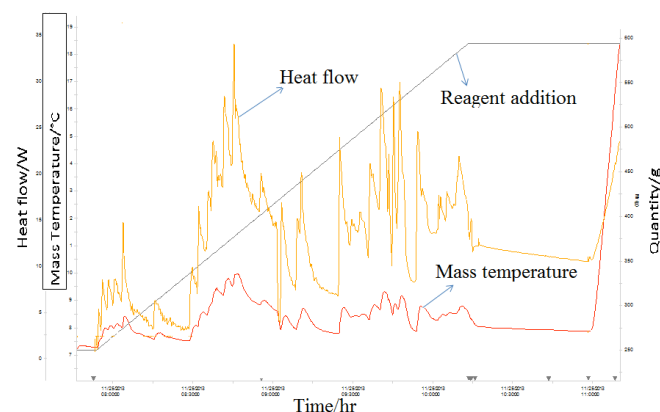


Figure 1: Heat flow profile for Fuming Nitric acid addition to 1, 3-Diethyl propanedioate at 7°C in RC1e.

MTSR value 120°C is more than the boiling point of Fuming Nitric acid, i.e., 83°C which stimulated us to go to the thermal stability experiment of reaction mixture in ARC.

1,3-Diethyl propanedioate and Fuming Nitric acid reaction mixture was heated at a ramp rate of 2°C min^{-1} , whereas the onset temperature of decomposition found in 60°C. Onset temperature decided based on starting point of deviation in the specified heating rate. i.e. $>2^\circ\text{C min}^{-1}$ at 60°C (Figure 4). The maximum temperature attained to 538°C within a few seconds once the decomposition triggers as shown in Figure 2 with a maximum self-heat rate of $4486^\circ\text{C min}^{-1}$ (Figure 3). Due to this high exothermic decomposition

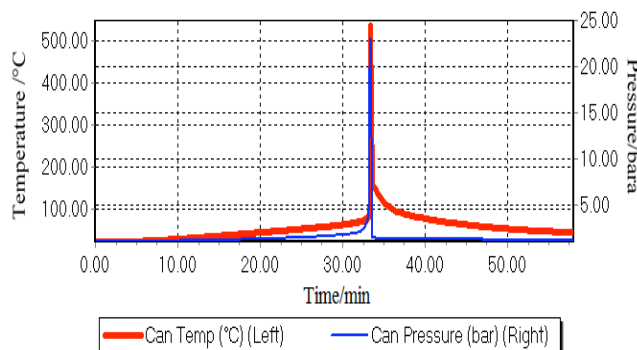


Figure 2: Temperature, Pressure versus Time plot of Reaction mixture.

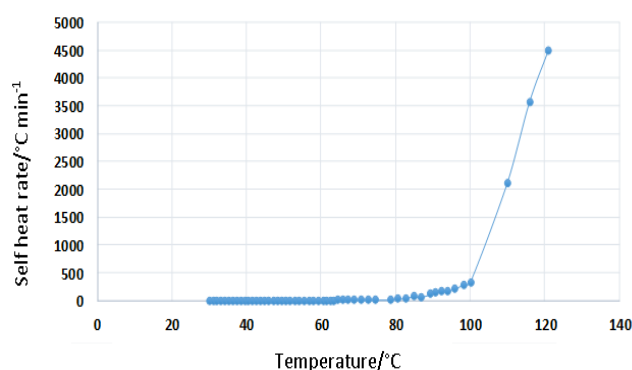


Figure 3: Self heat rate (dT/dt) versus Temperature plot of Reaction mixture.

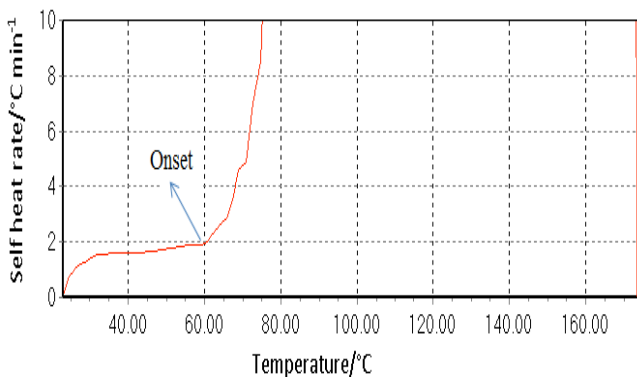


Figure 4: Zoomed Self heat rate (dT/dt) curve to identify the accurate onset temperature.

[19-21], pressure generation is too high and Hastelloy test cell which was used for experiment got ruptured. The recorded maximum pressure rise was 23 bara (Figure 5) by the pressure transducer which was not correct. Thermocouple data show the continuity in temperature data log, whereas the maximum pressure rise and maximum pressure-rising rate (397 bar min^{-1}) were not correct due to non-continuity in the data log

because of the test cell rupture. Photographs after completion of the experiment, i.e. rupture of test cell which was shown in Figure 6.

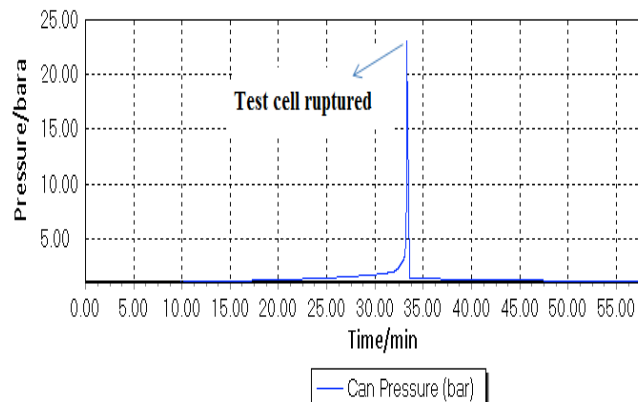


Figure 5: Pressure rise due to exothermic decomposition which resulted in test cell rupture.

Viewing of these experimental results, as per the desired conditions the maximum temperature of the reaction in the worst case scenario can reach till 120°C from the RC1e data, but there was an exothermic decomposition of the reaction mixture at onset of 60°C as per the ARC data which was undesired. Hence, it is high risk in terms of safety aspects. Apart from this, we also investigated about this exothermic decomposition is due to 1,3-Diethyl propanedioate or Fuming Nitric acid or only in case of mixed. Boiling point of 1, 3-Diethyl propanedioate is 199°C indicates it is stable till that temperature, which is more than MTSR value 120°C . Fuming Nitric acid alone tested in ARC by heating till 200°C (Figure 7) In a closed test cell. There was no exothermic event observed till 200°C . From this experimental evidence, concluded as the thermal decomposition occurs only to the reaction mixture.

4.1. Kinetics, T_{D24} and Criticality Class Index Evaluation

The desired reaction temperature is at 7°C and the onset temperature of the reaction mixture is at 60°C , so there is a possibility of reaching the reaction temperature to onset temperature due to its reaction heat in case of abnormal conditions of Fuming Nitric acid. Hence, it is essential to know the further information like T_{D24} [3] i.e., the temperature at which reaction mass is thermally stable for 24 hr and Criticality class (Figure 8) evaluation to know how severe the reaction is.

$$\ln(k_2/k_1) = (E_a/R) \cdot (1/T_1 - 1/T_2) \quad (1)$$



Figure 6: Photographs of the ARC equipment after test cell rupture.

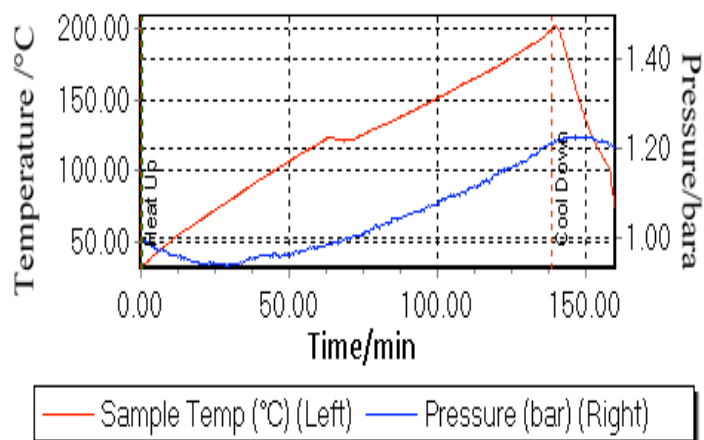


Figure 7: Temperature and Pressure profiles while heating of Fuming Nitric acid.

where R is Universal gas constant ($0.008314 \text{ kJ mol}^{-1}$), k_1 (0.0001 s^{-1}) is the rate constant at T_1 (60°C) and k_2 (1.4 s^{-1}) is the rate constant at T_2 (538°C). The activation energy (E_a) [22-24] is estimated as 41.6 kJ mol^{-1} .

Accordingly, T_{D24} value estimated by using at which adiabatic time-to-maximum-rate is 24 hours by an iterative procedure by changing the heat-releasing rate (Q') depends on temperature. T_{D24} value is 39°C at which the reaction mixture is unproblematic for at least 24 hours.

$$\text{TMR}_{\text{ad}} = (C_p * R * T^2) / (Q' * E_a) \quad (2)$$

To understand the criticality of a reaction, Francis Stoessel's criticality class evaluation [3] is very important for the choice and adequate risk reducing measures by knowing the four parameters T_p , MTSR , T_{D24} and MTT . Here T_p is 7°C , MTSR is 120°C , T_{D24} is 39°C and MTT is 83°C (Considered boiling point of Fuming Nitric acid as MTT). After arranging in ascending order of these four parameters, $T_p < T_{D24} < \text{MTT} < \text{MTSR}$ which is falling into criticality class 5. As per this class 5, once the process is loss of control the reaction will be triggered into decomposition results in a

runaway situation rather than reaching its MTT and MTSR temperatures. So it is very important to redesign the process with the options like converting into semi-batch operation instead of batch operation or lot wise instead of a single lot. One of the options can be divided into lots to avoid the thermal decomposition due to its reaction heat. In this case, we elected lot-wise addition of the reagent after considering the safe margin temperature for operation accordingly estimated the number of lots for a safer design of the process.

4.2. How Many Lots and How to Decide?

It needs to be understood the proximate estimation of number of lots (N) of reagent addition, considering the process temperature, adiabatic temperature and onset decomposition temperature of reaction mixture. A safe margin temperature (T_m) must be subtracted from T_o and Whereas MTSR should be less than $T_o - T_m$ for every individual lot. Here, in case of ARC assumed safe margin temperature is 30°C.

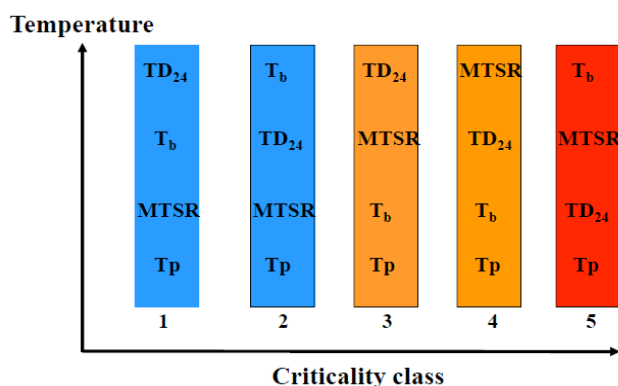


Figure 8: Criticality class index.

The number of lots can be estimated by the following formula in the case of uniform heat-releasing rate throughout the addition of the reagent

$$T_{\text{safe}} = T_o - T_m \quad (T_m = 30^\circ\text{C}) \quad (3)$$

$$T_p + (\Delta T_{\text{ad}}/N) = T_{\text{safe}} \quad (4)$$

$$N = \Delta T_{\text{ad}} / ((T_o - T_m) - T_p) \quad (5)$$

$$N = 113 / ((60 - 30) - 7) = \sim 5 \text{ lots} \quad (6)$$

As per this the total quantity of the reagent can be divided into 5 equal lots, where every individual lot is having the adiabatic-temperature-rise of 22.6°C ($\Delta T_{\text{ad}}/N = 113^\circ\text{C}/5 = 22.6^\circ\text{C}$). For every lot, the MTSR value will be 29.6°C ($T_p + (\Delta T_{\text{ad}}/N) = 7^\circ\text{C} + 22.6^\circ\text{C} = 29.6^\circ\text{C}$) in any worst case scenario, it will be less than

the onset decomposition temperature (60°C), T_{D24} value (39°C) and T_{safe} . In this modified lot-wise process, the criticality class index will fall in class 2. i.e. $T_p < \text{MTSR} < T_{D24} < \text{MTT}$. Hence we can consider the lot wise addition, to avoid the runaway situation in this reaction based on the experimental assessment of the reaction hazards, accordingly the process was scaled up and manufactured successfully.

CONCLUSIONS

The experimental hazard evaluation studies by using Reaction calorimeter (RC1e) and adiabatic reaction calorimeter (ARC) were helped us to understand the hazards of the process in case of both desired and undesired conditions. From the results, it was clear to understand that in case of loss of control during the reaction, it may end up with a runaway situation because the onset decomposition temperature of 1,3-Diethyl propanedioate and Fuming Nitric acid reaction mixture, i.e. T_o is less than the MTT and MTSR which indicates a high risk (Criticality class 5) involved in the process. These results were implemented in redesigning the process into a lot wise addition whereas reaction is controllable. An even worst case scenario also it may not trigger the runaway situation because the MTSR value of each lot is less than T_o , T_{D24} and MTT which indicates low risk (Criticality class 2).

Hence, these hazard assessment studies indicate the prominence of the experimental evaluation of the processes prior to scale up. Also, it is indicating that even critical reactions may be scalable once we know the hazard information which is more reliable and helps to take the necessary control measures at commercial scale operations.

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ABBREVIATIONS

M_r Quantity of the reaction mixture (kg)

C_p Specific heat capacity of the reaction mixture ($\text{kJ kg}^{-1} \text{K}^{-1}$)

Q_r	Total heat of reaction (kJ)
ΔT_{ad}	Adiabatic-temperature-rise ($^{\circ}\text{C}$)
T_o	Onset decomposition temperature ($^{\circ}\text{C}$)
T_{max}	Decomposition maximum temperature ($^{\circ}\text{C}$)
dT/dt	Self-heat rate ($^{\circ}\text{C min}^{-1}$)
dP/dt	Pressure-rising rate (bar min^{-1})
T_{safe}	Safe operational temperature ($^{\circ}\text{C}$)
T_m	Margin temperature ($^{\circ}\text{C}$)
T_{D24}	Temperature at which adiabatic time-to-maximum-rate is 24 hours ($^{\circ}\text{C}$)
T_p	Reaction or Process temperature ($^{\circ}\text{C}$)
Q'	Heat-releasing rate (kW kg^{-1})
E_a	Activation energy (kJ mol^{-1})
R	Universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) Pressure in bar absolute
k	Reaction rate constant (s^{-1})
TMR_{ad}	Adiabatic time-to-maximum-rate (s)
N	Number of lots
MTT	Maximum temperature for technical reasons ($^{\circ}\text{C}$)
$MTSR$	Maximum temperature of synthesis reaction ($^{\circ}\text{C}$)

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