

## **THERMAL HAZARDS EVALUATION FOR *sym*-TCB NITRATION REACTION USING THERMAL SCREENING UNIT (TS<sup>U</sup>)**

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(Received June 15, 2003; in revised form September 29, 2003)

### **Abstract**

A set of experiments was conducted in an HEL thermal screening unit with synthetic mixtures of raw materials in various proportions to evaluate the potential thermal hazards at normal and offset process conditions for nitration of symmetrical trichlorobenzene (TCB). The experiments were carried out in the adiabatic condition. The onset temperatures of the exotherms along with maximum temperature and pressure rise data for the desired and undesirable reactions were obtained. In the presence of excess nitric acid and oleum, the reaction shows a severe thermal runaway at the onset temperature of 138°C with a rapid rise in temperature and pressure leading to a potential explosion.

**Keywords:** nitration, *sym*-TCB, TCDNB, TCTNB, thermal runaway, TS<sup>U</sup>

### **Introduction**

The nitration of 1,3,5-trichlorobenzene (TCB) to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) is an intermediate step in the synthesis of insensitive high explosive, 1,3,5-trinitro-2,4,6-triaminobenzene (TATB) and the reaction is carried out at an elevated temperature (150°C) using a mixture of conc. nitric acid and oleum as nitrating agent [1–3]. The reaction is exothermic [4]. Sometimes reaction exothermicity and autoaccelerating behaviour can generate the occurrence of a runaway reaction [5–7]. Earlier, thermal hazards study for *sym*-TCB nitration reaction was carried out in this laboratory using DSC by Mandal *et al.* [8]. DSC study determined the heat of reaction and onset temperature for the decomposition of TCTNB at normal process conditions. The exothermicity involved in the nitration reaction with conc. H<sub>2</sub>SO<sub>4</sub> and nitric acid (70%) as nitrating agent was also investigated. However, DSC data have certain limitations such as absence of pressure data and rate of energy released. The extent of the thermal hazards is directly related to the pressure developed in the reaction and the rate of heat release. The Thermal Screening Unit (TS<sup>U</sup>) provides a quick and reliable technique for these measurements. In the present

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study, the reaction was investigated in an HEL TS<sup>U</sup> to supplement the thermal hazards potential evaluated in DSC.

## Experimental

### Materials

Oleum (20% SO<sub>3</sub> content) and conc. nitric acid (98%) were obtained from High Explosive factory, Kirkee, Pune, India. TCB (99.8%) was procured from Orion Chem. Pvt. Ltd. Mumbai, India.

### Methods

TS<sup>U</sup> with a spherical glass test cell of approximately 8 mL volume developed by the Hazard Evaluation Laboratory, U. K. was used for these experiments [9]. The schematic diagram of the TS<sup>U</sup> is shown in Fig. 1. The sample is contained in the test cell suspended in an oven. The oven, essentially a metal cylinder with a heating coil wrapped around the outer surface, is heated at a predefined rate. There are two temperature sensors to monitor the temperatures of the sample and oven during the course of the experiment. The sample temperature follows the same rate with slight offset. The test cell is also fitted with a pressure transducer to record the pressure developed inside. When an exotherm is detected, the sample temperature deviates from the background heating rate identifying the onset temperature of exotherm. The rate of sample temperature rise and the maximum value reached (before returning to the background rate), reveal important characteristics of the exotherm.

200 mg of TCB was mixed with oleum and conc. nitric acid in the predefined molar ratio in the glass test cell. The sample was heated at rate of 1 and 2°C min<sup>-1</sup>. Temperatures between 260 and 280°C and pressures between 16 and 20 bars were set as the maximum limits of experiment before the run. When the sample temperature or pressure crosses this set point the heating stops. The temperature and pressure were

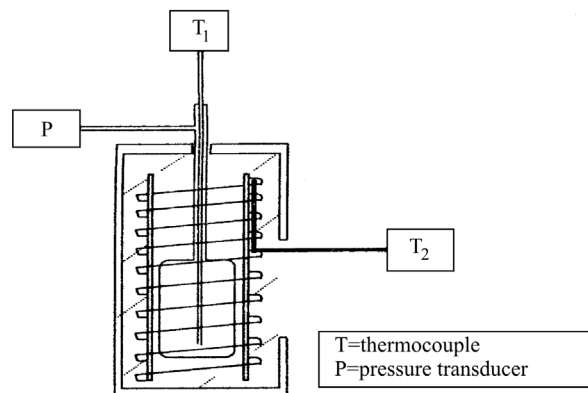


Fig. 1 Schematic diagram of TS<sup>U</sup>

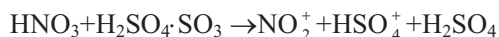
recorded during the run. Deviation from linearity (e.g. a sharp rise) indicates the 'onset' of an exotherm. The subsequent rise shows the severity of hazards, which were recorded in the graphical form. By analysis of these graphs the following information was obtained.

1. On-set temperature of exotherm.
2. Rate of temperature rise.
3. Rate of pressure rise.
4. Maximum temperature and pressure.
5. Time to explosion.

## Results and discussion

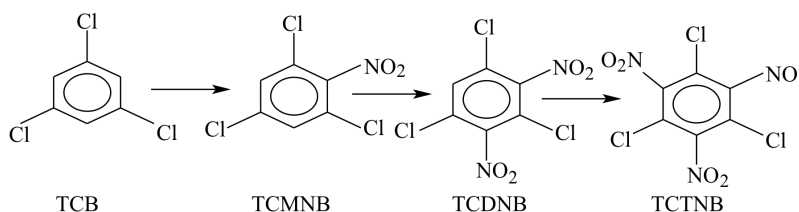
### *Effect of heating on standard molar ratio of reactants*

The nitration of TCB is a consecutive reaction as was investigated by previous authors [1–4, 8, 10, 11]. The acid mixture provides nitronium ion electrophile as shown in Scheme 1.



Scheme 1

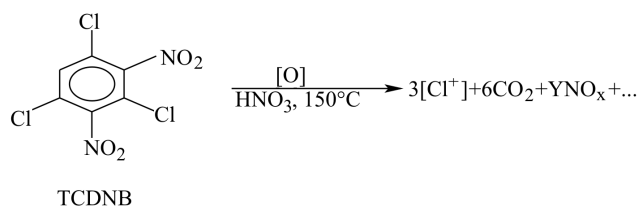
TCB is first converted to a mononitro derivative 1,3,5-trichloro-2-nitrobenzene (TCMNB), subsequently to 1,3,5-trichloro-2,4-dinitrobenzene (TCDNB) and finally to TCTNB (Scheme 2).



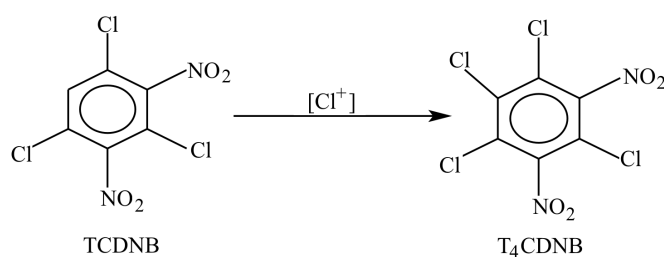
Scheme 2

The first nitration step is spontaneous, the second one is fast and the third step is slow, as the aromatic ring is deactivated by –R effect of two nitro groups in TCDNB. In order to enhance the rate of third nitration step, the reaction is carried out at an elevated temperature (150°C). At this reaction condition, there are two undesired parallel reactions, besides the desired main reaction. The parallel reactions are shown in Schemes 3 and 4. The existence of parallel reactions was proved by the analysis crude TCTNB obtained from the nitration reaction. The analysis reveals the presence of two predominant impurities TCDNB and 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T<sub>4</sub>CDNB). One of these parallel reactions is highly exothermic as it involves oxidation of TCDNB

(Scheme 3). This parallel reaction may trigger a thermal runaway if the reaction parameters are not controlled properly. Moreover, the oxidation of TCDNB favours the formation of T<sub>4</sub>CDNB, which affects the yield and purity of the desired product.

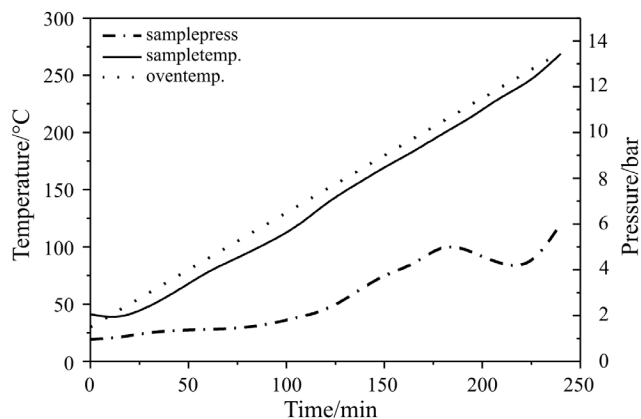


Scheme 3



Scheme 4

The standard molar ratio of reactants (TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:5.0:5.9) was taken for the first experiment. The sample was heated upto 260°C. The details of sample temperature, oven temperature and pressure are shown in Fig. 2. Any thermal runaway behaviour was not observed during the scan. A small endothermic hump at 130°C due to melting of intermediate TCDNB was found, which is only visible after enlargement of the TS<sup>U</sup> curve. Pressure in the system showed both upwards and down-

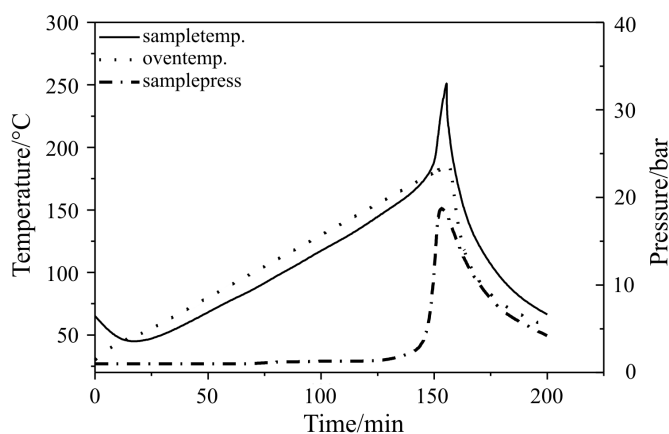


**Fig. 2** TS<sup>U</sup> expt. with standard reaction mixture [TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:5.0:5.9 (molar), heating rate 1°C min<sup>-1</sup>]

wards trends. It increased to 5.2 bars between sample temperatures 115 and 200°C and then showed a downward trend up to 4.0 bars at 245°C. Both temperature and pressure again showed an upwards trend at sample temperature above 245°C. This may be due to oxidation of TCTNB.

#### *Effect of excess nitric acid and oleum*

The mixture of TCB, conc. nitric acid and oleum (20%) was taken in a molar ratio of 1:6.8:8.5 (SO<sub>3</sub>) to study the effect of excess nitric acid and SO<sub>3</sub>. A detailed system response was recorded in the graphical form which is shown in Fig. 3. A clear runaway reaction was observed at the onset temperature of 138°C. The system went off as the sample temperature crossed the upper limit of 260°C. The rate of temperature rise is 36°C min<sup>-1</sup> and maximum temperature and pressure was greater than 267°C and 19 bar, respectively. The time required from exotherm initiation to explosion was 3.5 min.



**Fig. 3** TS<sup>U</sup> expt. with reaction mixture containing excess nitric acid and oleum [TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:6.8:8.5 (molar), heating rate 1°C min<sup>-1</sup>]

To understand the effect of each ingredient for these runaway behaviours, experiments were conducted separately with excess nitric acid (Fig. 4) and with excess oleum (Fig. 5). Both cases showed clear exothermicity at onset temperatures between 154 and 160°C. But the extent of exothermicity was different. In the case of excess oleum, greater exothermicity was observed which was indicated by the increase in sample temperature upto 270°C. This implies that oleum is more oxidising in nature than nitric acid. However, in both cases the sample temperature came down after some time and followed the oven temperature. The system pressure increased with the sample temperature in both cases. With excess nitric acid, the pressure increased to 11 bars between sample temperatures 155 and 218°C and finally reached a maximum of 18 bars at 275°C. In the case of excess oleum, the pressure increased to 15 bars with exothermicity and finally reached the maximum pressure of 22.2 bars at sample temperature 254°C.

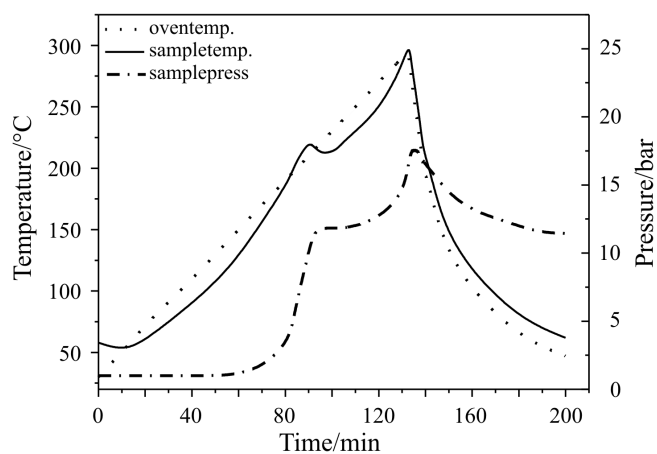


Fig. 4 TS<sup>U</sup> expt. with reaction mixture containing excess nitric acid [TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:6.8:5.9 (molar), heating rate 2°C min<sup>-1</sup>]

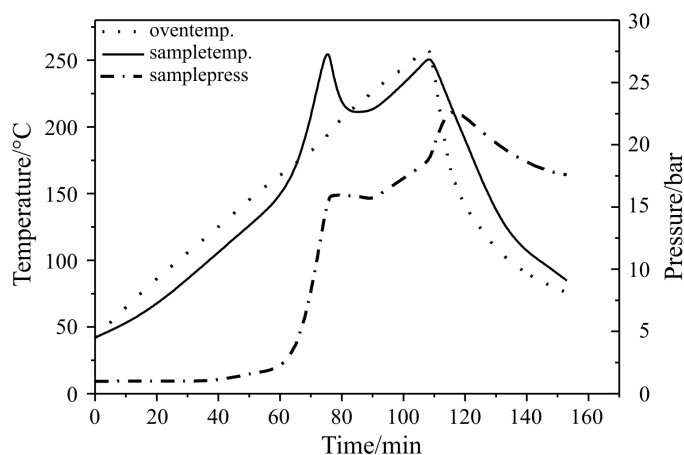


Fig. 5 TS<sup>U</sup> expt. with reaction mixture containing excess oleum [TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:5.0:8.5 (molar), heating rate 2°C min<sup>-1</sup>]

## Conclusions

Nitration of TCB should be preferably done in an open reactor since pressure develops in a sealed reactor. At standard molar ratio of TCB:HNO<sub>3</sub>:SO<sub>3</sub>=1:5.0:5.9, no thermal runaway behaviour was observed upto a reaction temperature of 225°C. The presence of excess nitric acid or oleum in TCB nitration process can initiate thermal runaway in the reaction temperature range 154–160°C. When TCB is nitrated in presence of excess amounts of both acids, a severe thermal runaway is initiated at 138°C with rapid rise in temperature and pressure leading to a potential explosion. Hence an appropriate molar ratio of reactants is not only important for optimum yield

and purity of the product TCTNB but also to prevent thermal runaway caused by highly exothermic oxidation reaction of TCDNB.

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Authors are thankful to Mr. V. L. Narasimhan, Associated Director, HEMRL for his valuable guidance and encouragement.

## References

- 1 M. E. Hill and F. Taylor, Jr., *J. Org. Chem.*, 25 (1960) 1037.
- 2 D. M. O'Keefe and F. T. Gurule, The Synthesis of Symmetrical Trichlorotrinitrobenzene, Part 1 – Nitrations with Alkali Metal Nitrates, Sandia Laboratories Report, Albuquerque, New Mexico, SAND 74-0112, June, 1977.
- 3 D. M. O'Keefe and F. T. Gurule, The Synthesis of Symmetrical Trichlorotrinitrobenzene, Part 2 – Nitrations with Nitric Acid; Synthesis of By-products, Sandia Laboratories Report, Albuquerque, New Mexico, SAND 78-1001, June, 1978.
- 4 W. T. Quinlin, Z. L. Estes, V. H. Evans and C. L. Schaffer, Pilot scale synthesis of TATB, Silas Mason Company Inc., Pantex Plant Report, MHSMP-76-20, July, 1976.
- 5 S. Korfmann, M. Wieczorek, L. Friedel, F. Westphal and H.-G. Schecker, *J. Therm. Anal. Cal.*, 58 (1999) 171.
- 6 G. Maschio, J. A. Feliu, J. Ligthart, I. Ferrara and C. Bassani, *J. Therm. Anal. Cal.*, 58 (1999) 201.
- 7 T. C. Ho, Y. S. Duh and J. R. Chen, 'Case Studies of Incidents in Runaway Reactions and Emergency Relief', *Process Safety Progress*, 17 (1998) 259.
- 8 A. K. Mandal, R. K. Syal and V. V. Bhujle, *Indian J. Environmental Protection*, 22 (2002) 377.
- 9 R. D. McIntosh and S. P. Waldram, *J. Therm. Anal. Cal.*, 73 (2003) 35.