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Effect of temperature and selected additives on the decomposition “onset” of 2-nitrotoluene using Advanced Reactive System Screening Tool

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A B S T R A C T

2-nitrotoluene (2-NT) is an important industrial chemical. However, in the past 25 years, serious incidents owing to its thermal decomposition have killed 10 people and injured more than 200. This research focuses on the thermal decomposition of 2-NT using the Advanced Reactive System Screening Tool (ARSST) to better understand the mechanisms that result in its explosion. Key parameters such as “onset” temperature, “onset” pressure, self-heat rate, and pressure rate are were studied. The influence of certain additives were investigated on these parameters. The results show the 2-NT decomposition reaction goes through two macroscopic decomposition stages, the first having an “onset” of around 300 °C and the second at about 400 °C. Unfortunately, part of the substrate evaporates during measurements with this technique, thus it was impossible to evaluate the enthalpy of the reaction and the effect of the sample size on the rate of decomposition or kinetic parameters. Additives such as Na_2SO_4 or $NaNO_3$ increased the decomposition “onset” temperature by approximately 30 °C, while KOH or NaOH reduced it by over 100 °C.

1. Introduction

The U.S. Environmental Protection Agency (EPA) lists 2-nitrotoluene (2-NT) as a high production volume chemical, with U.S. production between 10 and 50 million pounds during 1986–2002 (US EPA, 2004). According to 2010 data, it was produced by 10 companies in the U.S.A, seven companies in the People's Republic of China, three companies in the United Kingdom, two companies in Canada, and six other companies, one in each of the following countries: Czech Republic, Germany, India, Italy, Japan and Switzerland (Chem Sources, 2010). 2-NT is the raw material for the production of dinitrotoluene. Pure 2-NT can also be consumed by smaller specialty markets, such as the production of dyes, rubber and agricultural chemicals (Gattrell, 2013). It is a combustible, but difficult to ignite chemical (NIOSH, 2016) that will decompose under certain conditions, including elevated temperature, presence of impurities, and if maintained at moderate temperatures for an extended period of time. Fatal incidents involving the thermal decomposition of 2-NT have occurred and are shown in Table 1.

The thermal decomposition of 2-NT has been studied using different types of calorimetry. Ando et al. (1991) used several milligrams of 2-NT at 3.5 MPa in a Differential Scanning Calorimeter (DSC) and reported a detected onset of decomposition at 338 °C and a heat of decomposition of −1.32 kJ g^{-1}. In similar DSC tests, Duh et al. (1997) observed a detected onset temperature of 290 °C and a heat of decomposition of −2.40 kJ g^{-1}. Employing accelerating Rate Calorimetry (ARC) Sachdev and Todd (2005) measured a heat of reaction of −1.31 kJ g^{-1} and detected the onset temperature of 250 °C. However, in SAX's Dangerous Properties of Industrial Materials (Lewis, 1996), 2-NT may decompose explosively if heated above 190 °C. Bateman et al. (1974) performed isothermal tests at temperatures between 150 and 230 °C in a closed vessel and they found the isothermal induction period for the production of decomposition gas at 150 °C was 31 days.

The decomposition of 2-NT is rapid and highly exothermic. This is due to the following factors:

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Table 1
Incidents of fires or explosions caused by 2-nitrotoluene (Cutler and Brown, 1996; USCSB, 2004; China National Chemical Corporation, 2007).

Date	Location	Company	Injuries	Fatalities	Hazard	Cause
05/11/2007	Cangzhou, China	China National Chemical Corporation	80	5	Explosion (reactor)	Incompatible contamination
10/13/2002	Pascagoula, Mississippi	First Chemical Corporation	3	0	Explosion (distillatory)	Thermal decomposition
09/21/1992	United Kingdom	Hickson & Welch Ltd	181	5	Explosion (distillatory)	Thermal decomposition
08/07/1972	Institute, West Virginia	Union Carbide Facility	1	0	Explosion (pipeline)	External heat

(1) The decomposition occurs at higher temperatures (250–350 °C). Compared to other chemicals, *e.g.*, ammonium nitrate or organic peroxides, because its activation energy is higher, and as reported, endothermic reactions are more likely to happen (Galloway et al., 1994).
(2) The heat of decomposition is relatively high (>1.3 kJ g^{-1}). Consequently, under pseudo adiabatic conditions or at normal process conditions, the thermally-autocatalytic decomposition will accelerate due to the rapid temperature increase.

The decomposition mechanisms for nitro aromatic compounds are very complex. For 2-NT, 3 different initial pathways are proposed (Galloway et al., 1994; Gonzalez et al., 1985; Tsang et al., 1986; Matveev et al., 1978). The primary decomposition pathways are shown in Fig. 1. C-NO_2 homolysis is considered a dominant decomposition pathway of 3- and 4-nitrotoluene, and also occurs for 2-NT. Evidence of the nitro-nitrite rearrangement of 2-NT exists primarily in the gas phase and dilute solution. In the condensed phase, evidence is circumstantial (Brill and James, 1993). Several studies prove the C-H alpha attack is a primary decomposition pathway for TNT, 2,4-DNT, and 2-NT (Brill and James, 1993; Dacons et al., 1970; He et al., 1988). A summary of the kinetic data for each step is shown in Table 2.

During the manufacturing process, after the nitration step, nitro organic compounds are separated from the acid phase and washed to remove acids and water-soluble impurities (Gustin, 1998). Sodium sulfate, sodium nitrate, sodium hydroxide, and potassium hydroxide are the possible contaminants in the system. This work examined the thermal stability of 2-NT in the presence of these additives.

In order to propose inherently safer processing methods for nitrotoluenes and prevent incidents, more studies need to be conducted to fully understand their thermal behavior. In this work, the thermal decomposition of pure 2-NT liquid was studied using an Advanced Reactive System Screening Tool (ARSST). This paper is the first to report the decomposition data of 2-NT using the ARSST. The reported parameters measured are important in the characterization of the thermal behavior of 2-NT, including the observed "onset" temperature (T_{onset}) and "onset" pressure (P_{onset}). The results provide thermal hazard information about 2-NT for process industries, thus helping them to establish effective emergency programs.

2. Experimental

2.1. Materials

2-Nitrotoluene ($C_7H_7NO_2$, Aldrich, ACS Reagent, 99+%) was used in this study without further purification. Additives examined in this study include: Sodium sulfate (Na_2SO_4, Aldrich, ACS Reagent, 99+%), Sodium nitrate ($NaNO_3$, Sigma Aldrich, ACS Reagent, 97+%), Sodium hydroxide (NaOH, Sigma, 98+%, pellets), Potassium Hydroxide (KOH, Aldrich, 99+%), and Pentadecane ($C_{15}H_{32}$, Aldrich, 99+%).

2.2. Advanced reactive system screening tool (ARSST)

The ARSST is a pseudo adiabatic calorimeter manufactured by Fauske and Associates, LLC. It consists of three major components: containment vessel, control box, and computer. The standard containment vessel (350 cm^3) holds an open test cell (typically 10 cm^3), cell heater, thermocouples, and an insulation assembly around the test cell. The containment vessel is attached to a

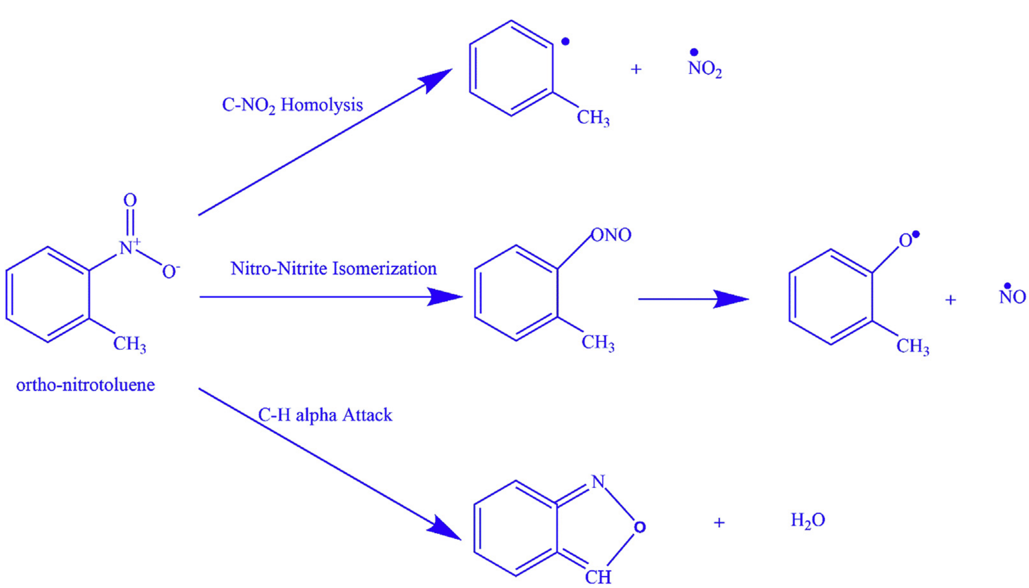

Fig. 1. Proposed decomposition pathways of 2-nitrotoluene.

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