



# Effects of inhibitor and promoter mixtures on ammonium nitrate fertilizer explosion hazards



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## ABSTRACT

Ammonium nitrate (AN) reactive hazards have been widely investigated for several years; however, incidents continue to occur. One of the most recent incidents occurred on April 17, 2013, where a fire led to an explosion at the West Fertilizer Company in West, Texas, USA. These incidents highlight the dire need for continuous research on AN hazards and alternatives to make its use safer. AN can thermally decompose and further detonate under certain conditions, *e.g.*, in the presence of impurities which act as promoters. However, certain additives can act as inhibitors and reduce the risk of its runaway. The main objective of the research presented here focuses on the synergistic effect of an inhibitor and a promoter on AN decomposition. The Reactive Systems Screening Tool (RSST) has been used in the study of the runaway behavior of AN in the presence of a promoter (KCl) and an inhibitor ( $\text{Na}_2\text{SO}_4$ ), and it is compared with the behavior of AN with each additive separately. It was found that when both additives are mixed,  $\text{Na}_2\text{SO}_4$  induces a rise in the decomposition "onset" temperature. The presence of KCl, however, induces a more violent decomposition worsening all other parameters. Potential decomposition mechanisms are also discussed.

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## 1. Introduction

Ammonium nitrate (AN) is widely used in both the fertilizer and explosives industries. Despite the fact that at ambient conditions AN is considered to be stable and relatively safe [1], fires and explosions associated with AN have occurred throughout history. This is because, under certain conditions (*e.g.*, presence of impurities), AN may behave as a strong oxidizing agent that can undergo detonation [2]. One recent incident occurred on April 17, 2013, in West, Texas, USA, in which approximately 30 t of stored AN exploded [3], killing 14 and injuring more than 200 people [4]. The blast wave completely destroyed the facility and also caused varying levels of damage to many buildings, businesses, and homes at significantly long distances from the plant. West Fertilizer Plant reported the presence of up to 270 t of AN at the site when the explosion occurred, and the plant also stored several other materials at the time of the explosion (according to its Tier Two report in 2013). Several other AN-related fires and explosion, such as the Texas City disaster in 1947 [5] and the Toulouse AN explosion in France in 2001

[6], also killed people and caused property damage. Contamination with other materials was believed to be one of the contributing factors to these incidents. Though the cause of the Toulouse disaster is still unclear, one potential reason is that AN contaminated with chloride (*i.e.*, sodium dichloroisocyanurate (DCCNa)) caused the explosion. Laboratory-scale experiment showed that AN–DCCNa mixture has higher decomposition rates than pure AN [6]. In another research [7], it is reported that moistened AN–DCCNa mixture could produce  $\text{NCl}_3$ , leading to the detonation of the mixture in the applied laboratory-scale.

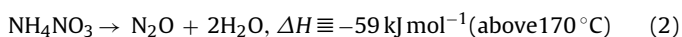
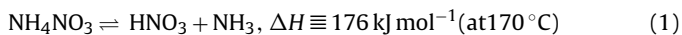
AN decomposition with a single additive has been widely studied in literature. This work focuses on AN mixed with two additives simultaneously. In literature, binary mixtures with AN have been studied mainly as explosives. Oxley et al. [1] obtained a relative ranking of the explosivity of energetic materials using the small-scale explosivity device (SSED) and compared SSED results with pipe bomb fragmentation data. They mixed AN with more than one additives, such as the mixture of ammonium sulfate, calcium carbonate, and urea. They found that low thermal stability was indeed related to high explosivity, but high thermal stability was no guarantee of low explosivity. Levchenko et al. [8] found the optimal for explosive composition of a three-component additive containing potassium salts and  $\text{Mg}(\text{NO}_3)_2$  as oxidizing agent. The effect of

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heating rate on thermal runaway was investigated by Boddington et al. [9] by mixing AN with ethylenediaminedinitrate and potassium nitrate to make explosive materials. AN was mixed with potassium nitrate and complexone salts in order to phase-stabilize AN as an oxidant by Klyakin and Taranushich [10]. In other publications, AN mixture with binary additives has also been reported. Klimova et al. [11] elucidated the thermodynamic effect of AN decomposition when mixed with Ca and Mg carbonates with or without the presence of boron, manganese, and copper compounds, such as AN mixture with CaCO<sub>3</sub> and CuSO<sub>4</sub>; CaCO<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub>; CaCO<sub>3</sub> and MnO<sub>2</sub>; *etc.* They found that equilibrium concentrations does not depend on the carbonate origin of CaCO<sub>3</sub>, MgCO<sub>3</sub>, or CaMg(CO<sub>3</sub>)<sub>2</sub>. In another research [12], AN was mixed with additives such as FeS and urea, FeS<sub>2</sub> and NaF, *etc.* Their conclusion was that salts of weak acids and urea stabilized AN formulations, even in the presence of destabilizing species.

The thermal decomposition of AN has been studied by various types of calorimeters, typically employing sample sizes of the order of a few milligrams and the data reported by different researchers have noticeable differences. The AN decomposition has been reported to start at various temperatures such as 210 °C [13], 200 °C [14], and 190 °C [15]. The detected “onset” temperatures of decomposition depend on the performance of the calorimeter. It must be emphasized that there is not really an “onset” temperature. According to Arrhenius law, reaction rates have an exponential dependency on temperature, reaction rates at low temperatures are very slow [16], and our ability to “detect” when a reaction “starts” depends on the sensitivity of the employed experimental equipment. The so-called “onset” temperature only marks the temperature at which the thermal effects caused by the reaction become detectable by the employed equipment. Due to different levels of accuracy of different equipment as well as testing methods, the detected “onset” temperatures of AN decomposition vary.

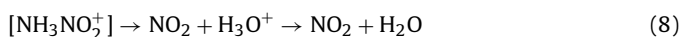
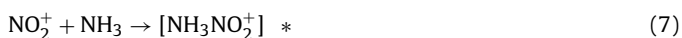
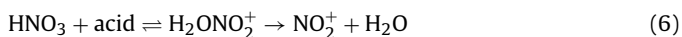
Different macroscopic AN decomposition paths have also been proposed and reported. The paths that attract more attention are listed below [17], in reaction (1) and (2). It needs to be pointed out that the products of AN decomposition are not limited to NH<sub>3</sub>, HNO<sub>3</sub>, N<sub>2</sub>O, and H<sub>2</sub>O. Several other gaseous products can also be generated, including N<sub>2</sub>, O<sub>2</sub>, NO, and NO<sub>2</sub> [17].



The generally accepted mechanism of AN decomposition is that the dissociation of HNO<sub>3</sub> leads to the subsequent oxidation of NH<sub>3</sub> [18], *e.g.*, Rosser et al. [28] proposed reaction (3) as the dissociation reaction of HNO<sub>3</sub>, which generates NO<sub>2</sub><sup>+</sup>, acting as the oxidizing species for NH<sub>3</sub> as listed in reaction (4). Reaction (5) shows a more realistic reaction path of HNO<sub>3</sub> decomposition [18].



To explain reaction (3) and (4) in more detail, in the presence of water, using “acid” to indicate NH<sub>4</sub><sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, or HNO<sub>3</sub>, the following decomposition mechanism equations (6)–(8) have been proposed [15], where reaction (7) is considered the controlling step due to its slow reaction rate.



Reaction (7) is also described in terms of elementary reactions in the literature [19] at the temperature range 342–387 °C, where NO<sub>2</sub><sup>+</sup>

subsequently oxidizes NH<sub>3</sub>, as listed in reactions (9)–(14). Reaction (15) is the overall stoichiometry according to this theory.



Slightly different from the previously mentioned mechanism, another approach [20] assumes that the formation of a nitramide intermediate out of AN results in the decomposition of AN, as listed in reactions (16)–(20).



In this study, the thermal decomposition of AN with two additives together (sodium sulfate and potassium chloride) has been studied using a Reactive System Screening Tool (RSST). The results are compared with pure AN test data, and with experimental data of AN in the presence of only one inhibitor (sodium sulfate) or one promoter (potassium chloride) in the same mass concentration. In runaway reactions, the hazard does not vary linearly with the amount of reactant. Therefore, it is important to determine if the reaction follows a trend upon scale-up. As a result, it is essential to evaluate reactive hazards with different sample sizes. This work reports AN experimental data obtained by the RSST, a pseudo adiabatic calorimeter, with sample sizes three orders of magnitude larger than the DSC. The determination of thermo-kinetic parameters, heat transfer, and safety data can be achieved by the use of different calorimetric techniques [21].

The importance of the scale up of laboratory data has been strongly addressed by Maschio et al. [21], where an integrated calorimetric approach was used to represent an efficient methodology to analyze and develop complex chemical processes. According to the authors, DSC, as a micro-calorimeter, has been used for the determination of fundamental thermo-kinetic process parameters. However, DSC data are not comparable with large-scale reactors, because the heat exchange capacity decreases as the reactor volume increases and the DSC data are usually obtained under conditions far from what is employed in industrial processes. Generally speaking, industrial runaway reactions are nearly adiabatic [22]. Additionally, thermodynamic data from adiabatic calorimeters, like adiabatic temperature rise and maximum pressure, can help determine process design parameters [22]. As a result, other reaction calorimeters such as RSST should be utilized to better study reactions, which can provide more realistic information than a DSC.

## 2. Experimental and analytical

### 2.1. Chemicals

Ammonium nitrate (VWR Reagent, ACS Grade, 99.9% assay), Sodium sulfate (Aldrich, 99+%, ACS Reagent), and Potassium chloride (Sigma, powder, Bio Reagent, 99.0+%) were used without further purification. Nitrogen (Acetylene Oxygen Co., Compressed

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