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# Thermal decomposition hazard evaluation of hydroxylamine nitrate

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**Abstract**

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine family and it is a liquid propellant when combined with alkylammonium nitrate fuel in an aqueous solution. Low concentrations of HAN are used primarily in the nuclear industry as a reductant in nuclear material processing and for decontamination of equipment. Also, HAN has been involved in several incidents because of its instability and autocatalytic decomposition behavior.

This paper presents calorimetric measurement for the thermal decomposition of 24 mass% HAN/water. Gas phase enthalpy of formation of HAN is calculated using both semi-empirical methods with MOPAC and high-level quantum chemical methods of Gaussian 03. CHETAH is used to estimate the energy release potential of HAN. A Reactive System Screening Tool (RSST$^{TM}$) and an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC$^{TM}$) are used to characterize thermal decomposition of HAN and to provide guidance about safe conditions for handling and storing of HAN.


*Keywords:* Hydroxylamine nitrate; APTAC; Screening methods; Autocatalytic reaction; Thermal decomposition

## 1. Introduction

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine family. High concentrations of HAN are used as liquid propellants, and low concentrations of HAN are used primarily in the nuclear industry for decontamination of equipment. Due to its instability and autocatalytic decomposition behavior, HAN has been involved in several incidents [1]. Therefore, the thermal stability and decomposition pathway of HAN in water are of interest. Several groups have investigated the kinetics and mechanism of HAN decomposition using various techniques and under different conditions [2–5]. However, due to its highly exothermic and rapid decomposition behavior, these studies could not provide complete information about the decomposition process. In this work, the thermal decomposition hazard of HAN is evaluated using both theoretical and experimental methods.

## 2. Theoretical screening methods and results

On May 14, 1997, an incident occurred in the Chemical Preparation Room of the Plutonium Reclamation Facility at the U.S. Department of Energy (DOE) Hanford's Plutonium Finishing Plant. The explosion destroyed the HAN storage tank and the room, and residual plutonium leaked from the building as wastewater [6]. During the investigation, it was determined that the root causes of the incident were inadequate hazard evaluation, inadequate auditing of safety management systems, and inadequate training of personnel on reactive hazards [7].

A systematic approach was proposed to evaluate reactive chemical hazards [8]. The first step of hazard evaluation is to use simple screening tools. For reactivity screening, Molecular Orbital Package (MOPAC) and ASTM Chemical Engineering Thermodynamics and Hazard Evaluation (CHETAH) are proven to be reliable and practical tools based on the analysis of the 167 incidents reported by Chemical Safety and Hazard Investigation Board (CSB) [9].

In this study, the semi-empirical quantum mechanical method MOPAC was employed to calculate the heat of for-

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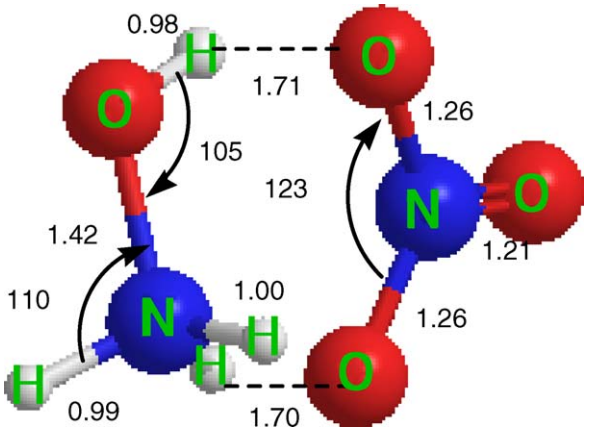


Fig. 1. The optimized gas phase structure of hydroxylamine nitrate.

mation of HAN at the level of theory of AM1 [10] and PM3 [11]. The optimized structure of gas phase HAN is shown in Fig. 1. The calculated gas phase heats of formation at 298 K are −64.8 and −57.8 kcal/mol using AM1 and PM3, respectively. In order to validate the results, the high level quantum mechanical method G2MP2 [12] from the Gaussian 03 suite of programs [13] was also used to calculate the heat of formation of HAN. The detailed method of calculating heat of formation is described in a Gaussian Whitepaper [14]. The obtained heat of formation of −61 kcal/mol is about the average of the results using the AM1 and PM3 methods.

The energy release potential of HAN decomposition was evaluated by the ASTM CHETAH program, in which the gas phase heat of formation of −61 kcal/mol was used as an input. The maximum heat of decomposition of HAN was estimated to be −57.1 kcal/mol with the final products of nitrogen, nitric acid, and water, as shown in Eq. (1). CHETAH provided a hazard classification of MEDIUM, but the overall energy release potential is HIGH. Therefore, further experimental study is necessary for the hazard evaluation of HAN decomposition to measure the temperature and pressure profiles.

$$NH_2OH \cdot HNO_3 \rightarrow 0.8HNO_3 + 0.6N_2 + 1.6H_2O \quad (1)$$

## 3. Experimental

### 3.1. Sample

Hydroxylamine nitrate (24 mass% in water solution, Aldrich catalog number 438235) was used without further purification and analysis.

### 3.2. Reactive System Screening Tool (RSST™)

The RSST, manufactured by Fauske & Associates, is a calorimeter for rapid measurement of reaction thermal behavior for temperatures up to 400 °C and pressures up to 500 psig. An open, 10 ml sample cell typically made of glass is placed inside a pressure vessel (400 ml) that can withstand pressures up to 500 psig. The RSST can be used not only for screening the reactive chemicals, but also for designing emergency relief devices. In this paper, glass thermocouples and polymer coated magnetic stirrer bars were used to provide a metal-free environment for the reactions. A fixed heating rate of 1 °C/min was used for temperatures up to 400 °C. The shutdown pressure limit was 450 psig. Initial nitrogen pressures of 250 psig were used to reduce material loss from the sample cell.

### 3.3. Automatic Pressure Tracking Adiabatic Calorimeter (APTAC™)

Adiabatic calorimetry has proven to be an extremely useful tool to assess thermal hazards of reactive chemicals. It can minimize heat losses by keeping the temperature of the sample surroundings close to the temperature of the sample. The APTAC calorimeter can be operated in a variety of test modes, such as Heat–Wait–Search, heat ramp, and isothermal aging with temperatures up to 500 °C and pressures ranging from vacuum to 2000 psia, and it can track exotherms at heat generation rates from 0.04 to 400 °C/min. It utilizes the DIERS pressure compensating technique in which the pressure outside the sample cell is controlled to match the pressure inside the sample cell. This allows use of a thin-wall sample cell which, when combined with the usual charge volume, can produce low thermal inertia data. For the present work, the measurements were conducted in glass sample cells of nominal 100 ml volume, which can provide a metal-free environment for the reactions, and also in titanium and stainless steel sample cells of nominal 130 and 50 ml volumes, respectively, to test the effect of metals on the thermal decomposition of HAN. Teflon coated thermocouples were used to prevent the contact of hydroxylamine solution with the metal thermocouple sheath.

The APTAC cannot measure heat of reaction directly, but the system of sample and sample cell was kept nearly adiabatic during runaway reaction. Therefore, part of the reaction heat was adsorbed by the sample cell, and the remainder was used to increase the temperature of the sample and vaporize the volatile materials. The fact that sample heat capacity changes with temperature, composition, and phase changes makes it more difficult to estimate the heat of the reaction from the experiment. Also, the liquid heat capacity of hydroxylamine nitrate is absent in the literature. However, because water was the solvent and a major product in this experiment, the heat capacity of liquid water (1 cal/(g °C)) was used to estimate the thermal inertia ($\phi = (M_sC_s + M_bC_b)/M_sC_s$, where $M$ is the mass, $C$ is the heat capacity and subscripts b and s refer to the sample bomb and the sample, respectively) and heat of reaction from the APTAC experimental results.