



# Thermal decomposition of hydroxylamine in aqueous solutions in the presence of NaCl, KCl or Na<sub>2</sub>SO<sub>4</sub> in the temperature range 120 °C–140 °C



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## ABSTRACT

The thermal decomposition of hydroxylamine aqueous solutions in two different concentrations and three temperatures was studied in the presence of NaCl, KCl and Na<sub>2</sub>SO<sub>4</sub> using isoperibolic calorimetry. The purpose of this study was to generate data for comparison of the thermal decomposition of different nitrogen containing compounds towards the ultimate, long-term goal to reveal the decomposition pathways of nitrogen containing species and to pinpoint the factors affecting these paths. It was found that Na<sub>2</sub>SO<sub>4</sub> was substantially reducing hydroxylamine decomposition rate, while the other two inorganic salts had a non-measurable effect on hydroxylamine decomposition rate. When NaCl and Na<sub>2</sub>SO<sub>4</sub> were used together the effect of the latter predominated. In all cases the non-condensable gas generation was not practically affected by the presence of any of the additives. The results were compared with the effect that KCl and Na<sub>2</sub>SO<sub>4</sub> had on ammonium nitrate thermal-decomposition rate and similarities and differences are discussed. It is believed that rate deceleration effects of Na<sub>2</sub>SO<sub>4</sub> are owing to the alkaline character of SO<sub>4</sub><sup>2-</sup> anion.

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## 1. Introduction

### 1.1. Proposed mechanisms of thermal decomposition of hydroxylamine

Hydroxylamine, NH<sub>2</sub>OH, is a thermally unstable energetic compound of increasing demand used in chemical synthesis, in the nuclear and semiconductors industries, as a rocket fuel, etc. It has been responsible for two serious accidents, one in Concept Sciences, Inc. Pennsylvania, USA, in 1999, which resulted in five fatalities and 14 injuries and one in Nissin Chemical Company, in Gunma, Japan, causing four deaths and 58 injuries (CSB, 2002; Long, 2004). Following these accidents, intensive research has been conducted on its thermal decomposition (e.g. Cisneros et al., 2001; Saraf et al., 2003; Yusaku et al., 2003; Cisneros et al., 2004a) and the factors affecting it (e.g. Cisneros et al., 2002; Cisneros et al., 2004b), like the hydroxylamine matrix and the presence of metal contaminants with emphasis on iron, a likely

culprit for the latter of the two aforementioned accidents (Cisneros et al., 2003; Yusaku and Koseki, 2003; Kumasaki, 2004). The kinetics of hydroxylamine decomposition and the effects of additives were of scientific interest decades before these accidents occurred (e.g. Luňák and Vepřek-Siška, 1974; Pembbridge & Stedman, 1979; Bremner et al., 1980). These older relevant studies, were apparently performed at ambient temperature at mild and controlled conditions (conditions are not always reported), where the effects of different factors can be easily measured and evaluated. Under runaway conditions, however, the products formed and the reaction pathways can vary as they are condition-dependent. The importance of the dependency on conditions and the need for relevant research was pinpointed by the aforementioned two tragic accidents.

This dependency on conditions is most likely the reason for which different and controversial mechanisms of hydroxylamine thermal decomposition have been proposed by researchers as reported by Wei et al. (2004) and the nature and role of the intermediates formed are in debate. Between others, hydroxylamine thermal decomposition depends on pH. It has been proposed that hydroxylamine thermal decomposition proceeds via reactions (1) and (2) following an initiation step via which hydroxyhydrazine

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forms, as shown in reaction (3). The addition of an alkali in an aqueous solution of hydroxylamine favors reaction (2) and acts as a catalyst to reaction (3); in the presence of an acid, reaction (1) predominates, while reaction (3) is inhibited. (Wei et al., 2004).



In both cases ( $\text{HONNH}_2$ ) was proposed to be formed as intermediate product, as follows:



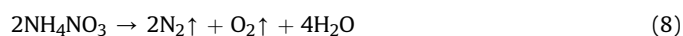
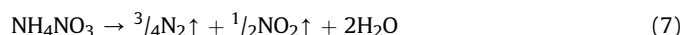
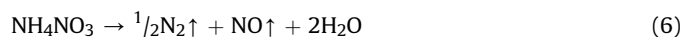
Conditions which affect the reaction runaway and the products formed depend on the presence of contaminants, the temperature history during the runaway, the sample size, the reaction environment, etc. Reactions during hazardous runaways release high amounts of thermal power, rising rapidly the reactor temperature and produce non-condensable gases at high rates. As such, only global reaction kinetics are usually studied experimentally; reaction mechanisms, product identification or quantification during reaction runaways is very difficult. Thus, inevitably, experimental research on those is to a large extent empirical. Consequently, for their study, and to enlighten the underpinning science, data from different sources have to be combined and correlated. Towards that objective, molecular simulations can play an important role. In a more recent study, Wang et al., 2010, have performed a theoretical study on the initial steps of hydroxylamine decomposition using computational chemistry. However, such studies need reliable experimental data. Therefore, measurements obtained from adiabatic calorimetry (larger samples) have to be combined with those of differential scanning calorimetry (very small samples) together with other forms of experimental and simulated data and to be examined through relevant theory, in order to provide integrated information on the evolution of a runaway. With this long-term objective in mind, in the present research we performed isoperibolic measurements on hydroxylamine decomposition in the presence of additives. Those measurements were performed at relatively high temperatures, employing a relatively high amount of hydroxylamine. Both, the temperature and the quantity of the samples, play an important role on the reaction pathways followed during hydroxylamine runaway. They are both difficult to be addressed experimentally and as such the research presented here is of a unique value. The additives employed were selected so that they could provide useful data for correlations with future results, which will be obtained from other nitrogen containing species. In particular, ammonium nitrate, (AN),  $\text{NH}_4\text{NO}_3$ , has already been studied with the use of similar additives, as reported later.

## 1.2. Proposed mechanisms of thermal decomposition of ammonium nitrate

Different decomposition mechanisms of AN have been reported in literature; the most accepted reactions are summarized in (Han et al., 2015). It is believed that the vaporization of melted ammonium nitrate leads to the formation of ammonia and nitric acid, which could then initiate the decomposition of ammonium nitrate through reaction (4)



At higher temperatures and/or under specific conditions reactions (5), (6), (7), (8) or (9) have also been proposed.



As can be seen, the decomposition of both ammonium nitrate and hydroxylamine can produce  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$ ,  $\text{NO}$ , or  $\text{NO}_2$  as potential intermediates or final products. Moreover, hydroxylamine is considered to be an intermediate in the reduction of nitric oxide to ammonia (Cisneros et al., 2003).

Therefore, as a motivation for the current study, it was opted to examine if the presence of each one of the selected additives had similar or distinct effects on the thermal decomposition of hydroxylamine and ammonium nitrate and to provide data for future scientific research on the reasoning and the correlation of the effects of additives on the thermal decomposition of different inorganic, nitrogen-containing compounds.

The thermal decomposition of AN was inhibited with  $\text{Na}_2\text{SO}_4$ ; more precisely  $\text{NH}_4\text{NO}_3$  decomposition “onset” was increased and the overall temperature increase was lower than the respective quantities of the pure ammonium nitrate. (Han et al., 2016). On the contrary, KCl reduced the decomposition “onset” and increased the adiabatic temperature rise, thus indicating that both the rate and the decomposition paths were affected by the presence of the additive (Han et al., 2016).

In the present study the effect of NaCl, KCl and  $\text{Na}_2\text{SO}_4$  on the rate and the non-condensable gas generation during hydroxylamine thermal decomposition was examined. The effect they have on the decomposition of AN is compared with that on hydroxylamine and the role of the anion and the cation on the rate of hydroxylamine decomposition is discussed.

## 2. Materials and methods

All reagents were used without any further purification. The reagent employed, hydroxylamine (Fluka 55458 purum, ~50% w/w in  $\text{H}_2\text{O}$ ) was diluted with ultra-pure water so as to form approximately 40 mL of solution. The quantities of reagent employed were ca. 5 or 10 g; the exact quantities employed in the present study are shown in more detail in Table S1 of the supplementary materials. In each of the measurements shown in Table S1, sufficient ultra-pure water was added so as to make a 40 mL solution at 22 °C. Solid NaCl (Riedel-deHaen 99.8%), KCl (Sigma-Aldrich 99.5%) and/or  $\text{Na}_2\text{SO}_4$  (Sigma-Aldrich 99.5%) were used as additives. They were added in identical molar concentrations or in multiples of the selected molar concentration.

Hydroxylamine decomposition was studied isoperibolically at 120 and 140 °C using a 316 SS metal vessel of a capacity of 150 mL as a reactor (Swagelok double ended 316L SS/DOT-3E 1800 TC-3EM 124-Product code 316L-HDF4-150) in a similar way as described in our previous work Adamopoulou et al., 2012. For the isoperibolic temperature stability the reactor was submerged in a Julabo FP50-HD, 2.9 kW oil system with a temperature stability of  $\pm 0.1$  °C. The reactor temperature was measured by a PT(a)100 platinum resistance thermometer. Pressure was measured by means of an Omega Engineering 30–300 psi pressure gauge with a readability of 5 psi for measurements. The experimental procedure was as follows: If an additive was used its selected quantity was dissolved in water. The mass of different additives was such that the molar concentration of additives in the solution was the same. Subsequently, the

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