# Isoperibolic study of hydroxylamine in aqueous solutions in the presence of selected inorganic salts

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## Abstract

The thermal decomposition of hydroxylamine aqueous solutions in two different concentrations and two temperatures was studied in the presence of KCl, NaCl and $Na_2SO_4$ using isoperibolic calorimetry.
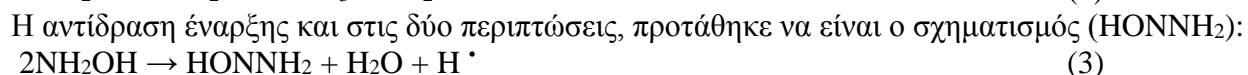
It was found that $Na_2SO_4$ was substantially reducing its decomposition rate, while the other two compounds had a rather insignificant influence on hydroxylamine decomposition rate.

The results are compared with the effect that the same salts have on ammonium nitrate decomposition rate and similarities and differences are discussed.

## Introduction

### Proposed mechanisms of thermal decomposition of hydroxylamine

Different mechanisms of hydroxylamine thermal decomposition have been proposed by researchers. 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 forms, as shown via reaction (3). The addition of an alkali in an aqueous solution of hydroxylamine favors reaction 2 and acts as a catalyst to reaction (3), while in the presence of an acid, reaction (1) predominates, while reaction (3) is inhibited. (C. Wei *et al.*, 2004).
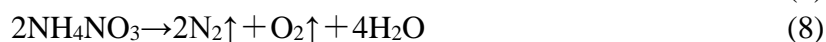
$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O \qquad (1)$$
$$4NH_2OH \rightarrow N_2O + 2NH_3 + 3H_2O \qquad (2)$$

Η αντίδραση έναρξης και στις δύο περιπτώσεις, προτάθηκε να είναι ο σχηματισμός ($HONNH_2$):

$$2NH_2OH \rightarrow HONNH_2 + H_2O + H^{\cdot} \qquad (3)$$

### Proposed mechanisms of thermal decomposition of ammonium nitrate

Different decomposition mechanisms of AN have been reported in literature of which 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)

$$NH_4NO_3 \rightleftharpoons HNO_3 + NH_3 \qquad\qquad (4)$$

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

$$NH_4NO_3 \rightarrow N_2O + 2H_2O, \qquad\qquad (5)$$
$$NH_4NO_3 \rightarrow 1/2N_2 + NO + 2H_2O \qquad\qquad (6)$$
$$NH_4NO_3 \rightarrow 3/4N_2 + 1/2NO_2 + 2H_2O \qquad\qquad (7)$$
$$2NH_4NO_3 \rightarrow 2N_2\uparrow + O_2\uparrow + 4H_2O \qquad\qquad (8)$$
$$8NH_4NO_3 \rightarrow 5N_2\uparrow + 4NO + 2NO_2\uparrow + 16H_2O \qquad\qquad (9)$$

As can be seen the decomposition of both compounds can produce $NH_3$, $N_2$ and $N_2O$, NO, or $NO_2$ as potential intermediate or final products. Therefore, it was decided to examine if the effect of additives on each of them is similar or not.

The thermal decomposition of ammonium nitrate was inhibited with $Na_2SO_4$; more precisely the decomposition "onset" was increased and the overall temperature increase was lower than those of the pure ammonium nitrate. On the contrary, KCl, reduced the decomposition "onset" and increased the 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 $Na_2SO_4$ was examined. They were selected in order to identify whether the effect they had on the decomposition of ammonium nitrate was similar with that on hydroxylamine and whether it was the anion or the cation which played the primary role on the decomposition rate and potential pathways.

**Materials and Methods**

All reagents were used without any further purification. Hydroxylamine (Fluka 55458 purum, ~ 50% σε $H_2O$) was diluted with ultra-pure water so as to form approximately 40 ml of solution. The quantities of ultra-pure water added are indicated in Table 1. Solid NaCl (Riedel-deHaen 99.8%), KCl (Sigma-Aldrich 99.5%) and/or $Na_2SO_4$ (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 isoperibilically at 120, 130 and 140 °C using a 316SS 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), filled with approx. 40 ml of solution . For the isoperibolic temperature stability the reactor was submerged in a Julabo FP50-HD, 2,9kW oil system with a temperature stability of +/- 0,1°C. The mass of different additives was such that the molar concentration of additives in the solution was the same. Each measurement was interrupted when the pressure rise was less than one psi in the course of a few hours.

The measurements performed are shown in Table 1.

**Results and Discussion**

Table 1 shows the measurements performed in this study. The first column shows the measurement code. The second, the reagent (50% hydroxylamine in water) mass. The next three columns show which salt was added and the subsequent three the isoperibolic temperature of the measurement. The two columns which follow show the final pressure reached at the temperature of the measurement and the pressure of non-condensable gases at ambient temperature,

respectively. In the last column the ratio of the pressure of non-condensable gases at ambient

| EXP | Reagent mass(g) | NaCl (g) | KCl (g) | Na$_2$SO$_4$(g) | 120 °C | 130°C | 140 °C | P$_{max}$ (psi) | P$_{f\_amb}$ (psi) | P$_{f\_amb}$/mass (min) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10.32 | | | | ✓ | | | 180 | 40 | 1.24 |
| 2 | 6.19 | | | | | ✓ | | 97 | 30 | 1.25 |
| 3 | 4.84 | 0.30 | | | ✓ | | | 85 | 40 | 2.63 |
| 4 | 5.35 | | | | ✓ | | | 85 | 45 | 2.85 |
| 5 | 10.74 | 0.61 | | | ✓ | | | 227.5 | 146 | 6.12 |
| 6 | 5.06 | 0.30 | | | ✓ | | | 107 | 59 | 4.40 |
| 7 | 5.05 | | 0.4 | | ✓ | | | 102.5 | 55 | 4.01 |
| 8 | 5.07 | | | | | | ✓ | 131 | 55 | 3.99 |
| 9 | 5.05 | 0.30 | | | | | ✓ | 132 | 55 | 4.01 |
| 10 | 5.14 | | 0.402 | | | | ✓ | 132 | 56 | 4.04 |
| 11 | 5.05 | | | 0.744 | | | ✓ | 126 | 57 | 4.21 |
| 12 | 10.27 | | | 2.98 | | | ✓ | 240 | 130 | 5.62 |
| 13 | 5.06 | 0.91 | | | | | ✓ | 136 | 57 | 4.20 |
| 14 | 10.06 | | | | | | ✓ | 240 | 140 | 6.24 |
| 15 | 10.02 | 0.60 | | | | | ✓ | 240 | 132 | 5.86 |
| 16 | 10.01 | | 0.8 | | | | ✓ | 240 | 130 | 5.77 |
| 17 | 10.07 | | | 4.44 | | | ✓ | 235 | 126 | 5.54 |
| 18 | 10.01 | 0.6 | | 2.986 | | | ✓ | 231 | 125 | 5.52 |

temperature, divided by the mass of hydroxylamine employed is shown.

Figure 1 shows the effect of the addition of NaCl on the final pressure of non-condensable gases generated during hydroxylamine decomposition at 120 °C (dotted bars) and at 140 °C (stripped bars) for different reagent masses. As can be seen in Figure 1, neither the temperature nor the additive has a measurable effect on the quantity of non-condensable gases generated during hydroxylamine decomposition. This plausibly indicates that the mechanism of its decomposition may not be altered by those factors. On the other hand, the mass of hydroxylamine has a pronounced effect on the quantity of the non-condensable gases generated. This is consistent with our previous findings (Adamopoulou et al 2012). So, the mass fraction of hydroxylamine in the solution is 0.0625 the gas generated per gram of reagent (50% hydroxylamine solution) is of the order of 4 psia (or 8 psia per gram of hydroxylamine).

Table 1. Hydroxylamine thermal decomposition results
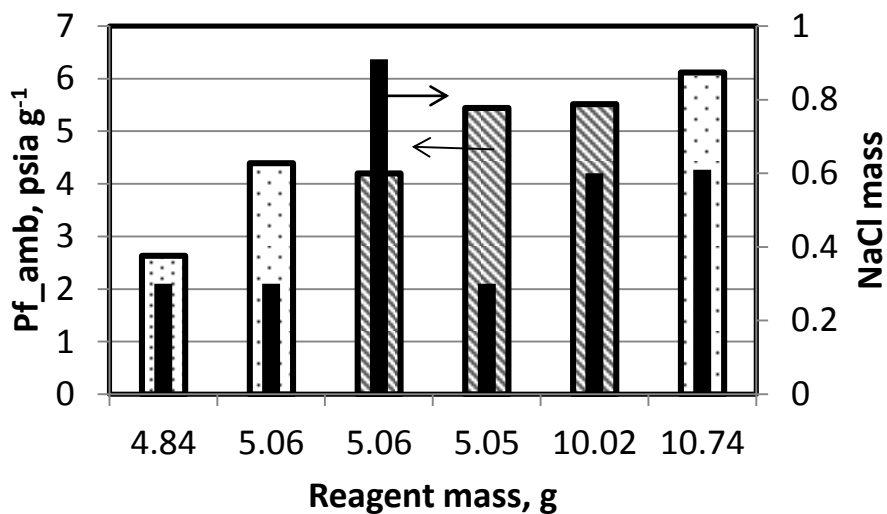
**Figure 1.** Effect of NaCl on the non-condensable gas generation during hydroxylamine decomposition. Stripped bars correspond to measurements taken at 140 ℃ while the dotted ones to 120 ℃
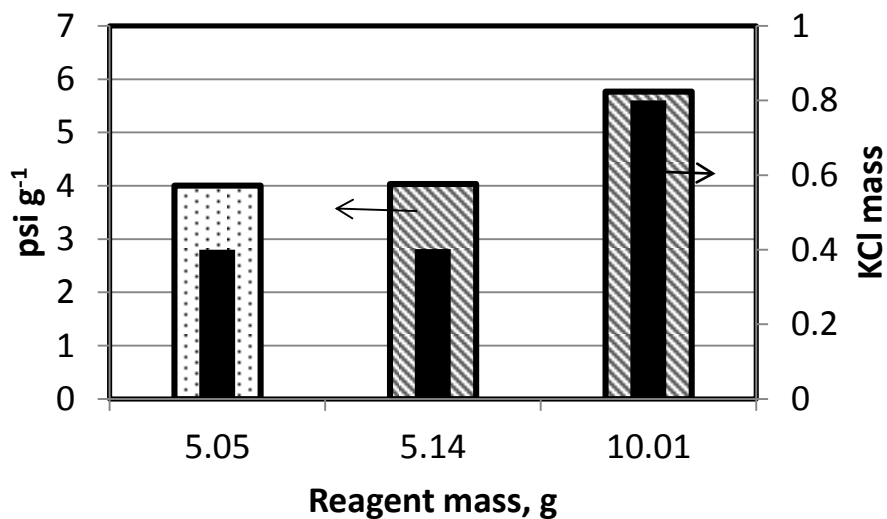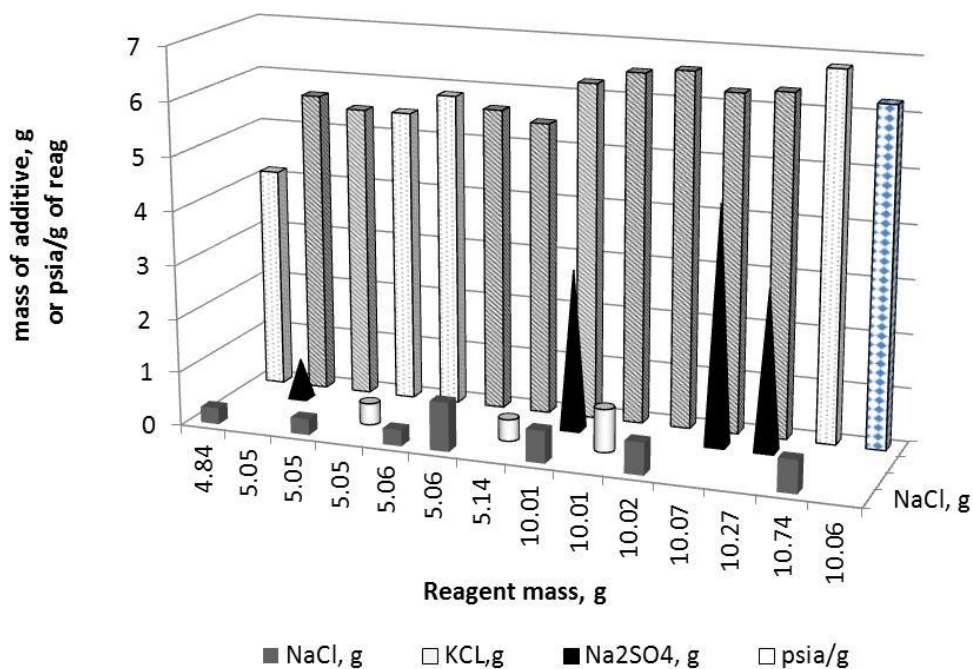


**Figure 2.** Effect of KCl on the non-condensable gas generation during hydroxylamine decomposition. Stripped bars correspond to measurements taken at 140 ℃ while the dotted ones to 120 ℃.

On the other hand, when the mass fraction of hydroxylamine is 0.125 the gas generated per gram of reagent (50% hydroxylamine solution) is of the order of 6 psia (or 12 psia per gram of hydroxylamine).

Similar results were found, and can be seen in Figure 3, in the measurements where KCl was been used as additive.

In Figure 3, a comparison is made between all additives. In one of the measurements, two additives have been used simultaneously. As can be seen in Figure 3, it is only the mass of hydroxylamine which plays the primary role in the pressure generation during hydroxylamine decomposition.

However, the rate of hydroxylamine decomposition seems to be affected by the presence of $Na_2SO_4$. Although the pressure generated during decomposition reaches the same value as that reached by hydroxylamine decomposition, the decomposition was substantially slower. On the other hand, the employed concentrations of NaCl or KCl, left the rate of decomposition unaffected.

Further measurements with larger concentrations of NaCl and KCl have to be tested before any firm conclusions are drawn. However, it is likely that it is the pH which mainly affects the process of decomposition.



**Figure 3.** Effect of NaCl, KCl and $Na_2SO_4$ on the non-condensable gas generation during hydroxylamine decomposition at 120 ºC and 140 ºC for *ca* 5 g and *ca* 10 g of reagent . Stripped bars correspond to measurements taken at 140 ºC while the dotted ones to 120 ºC. The last bar corresponds to hydroxylamine decomposition without any additives.
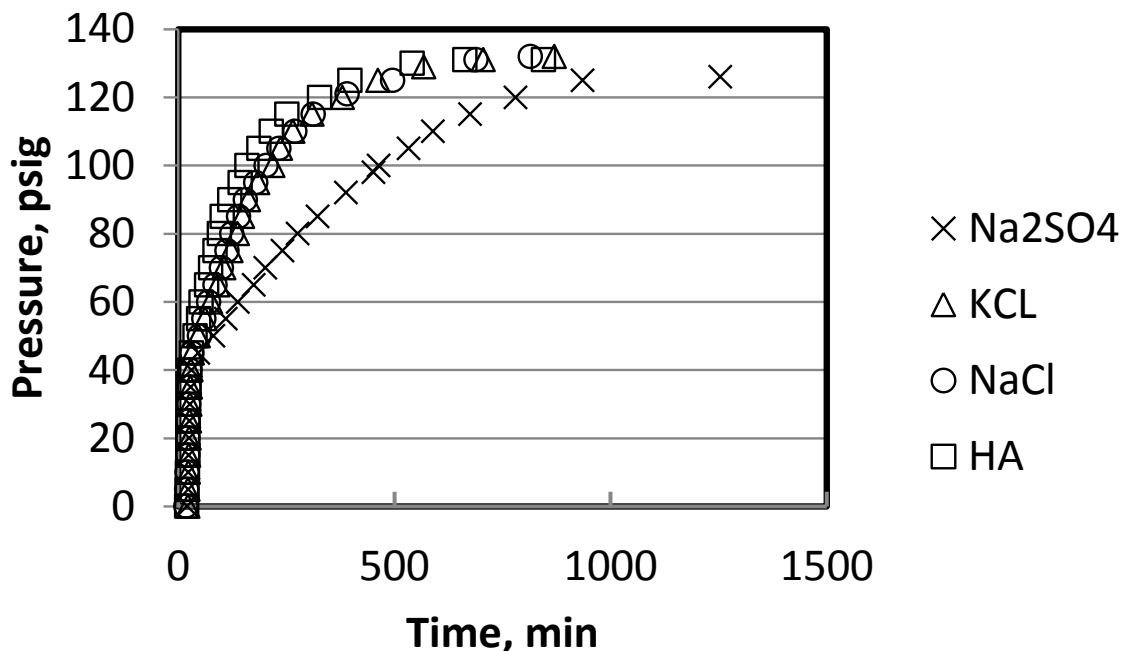
**Figure 4.** Effect of additives on the rate of decomposition.

**References**

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