



## Isothermal decomposition of hydroxylamine and hydroxylamine nitrate in aqueous solutions in the temperature range 80–160 °C

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### ABSTRACT

Hydroxylamine (HA) and hydroxylamine nitrate (HAN) have been involved independently in several tragic accidents, which incurred numerous fatalities and injuries. Following these incidents, adiabatic calorimetry and computational chemistry research was conducted on those compounds, suggesting potential reaction pathways of their decomposition, but the mechanism of their unstable behavior, still have not been completely understood.

In the present work, isothermal decomposition tests were performed accompanied with HPLC, ion chromatography and UV analyses in the temperature range 80–160 °C. Condition-dependent autocatalytic decompositions were demonstrated for HA and HAN, and an intermediate formation has been observed that is most likely responsible for their autocatalytic behavior. These findings corroborate previously reported computational chemistry results.

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### 1. Introduction

Since 1999, hydroxylamine has been involved in two tragic accidents [1,2], which incurred numerous fatalities and injuries. Following these two incidents, research on hydroxylamine has been conducted at the Mary Kay O'Connor Process Safety Center in the Chemical Engineering Department at Texas A&M University. The system has been subjected to adiabatic calorimetry tests, which have provided the temperature, pressure, and heat generation history of hydroxylamine decomposition under selected runaway conditions. Molecular modeling has been employed to elucidate the elementary reactions occurring during its thermal decomposition. Finally, based on the decomposition end products, the most likely of the potential reaction paths had been selected [3–5].

The research presented here targets development of a methodology for the isothermal kinetic study of the reaction and the measurement of its heat generation. The immediate targets of this research are:

(a) To establish the conditions that allow the reaction to proceed in the kinetic regime, which is not always possible with fast autocatalytic runaway reactions.

- (b) To establish practical and reliable methods of analysing liquid-phase and gas-phase products during the course of the reaction. This target is subjected to practical limitations given that high pressures can be developed during runaway reactions and the reactant mass employed in a measurement must be sufficiently small. Thus, the reactor employed cannot accommodate bulky probes, while samples withdrawn from the reactor must be very small.
- (c) To combine isothermal and adiabatic calorimetry and computational chemistry for the in-depth study of the mechanisms of hydroxylamine thermal decomposition.

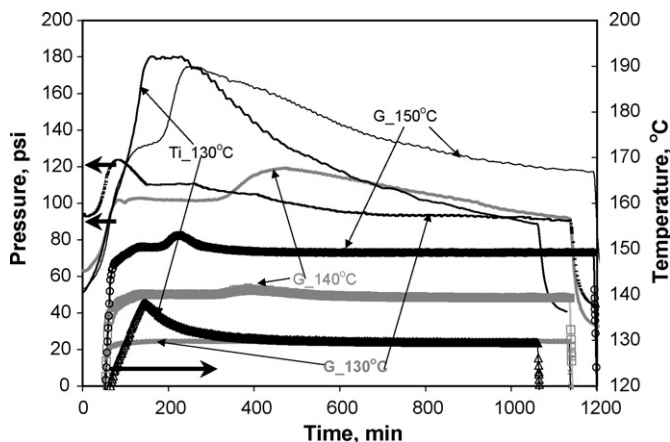
### 2. Experimental

#### 2.1. Materials and methods

Hydroxylamine isothermal decomposition measurements were performed in the temperature range of 80–160 °C using an HEL, UK, SIMULAR isothermal calorimeter equipped with an in-house made pressure-resistant glass reactor and an Arthur D. Little, USA, Adiabatic Pressure Tracking Calorimeter (APTAC) employing glass and titanium cells. Products were identified via UV, high performance liquid chromatography (HPLC), and ion chromatography (IC). HPLC measurements were performed using a Dionex, USA, P680 system with a Dionex 1024 dio-array detector equipped with an Acclaim C18 5 μm 120 Å, 4.6 mm × 250 mm column thermostated at 24 °C using a 95:5 water:acetonitrile isocratic mobile phase at

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**Fig. 1.** Pressure and temperature history of HA decomposition in aqueous solutions. G and Ti indicate glass or titanium cell. Plain lines show pressure variation (read on the left-hand axis), and lines with markers show temperature variation (read on the right-hand axis).

1 ml/min with UV detection at 201, 206, 210, 530 and 254 nm. IC measurements employed a Dionex, USA, ICS 1500 chromatograph equipped with AS9-Hc column, with a 9 mM sodium carbonate mobile phase. A Perkin Elmer, USA, lambda 35, UV spectrophotometer was employed for the UV analyses. Samples of 3 ml held in quartz cuvettes were tested over the entire 800–190 nm range of the UV instrument.

## 2.2. Reaction conditions

Reactions were performed in the temperature range of 80–160 °C using a SIMULAR isothermal calorimeter with an in-house made, small glass reactor, which could withstand a pressure of 6 bar-a. Measurements were also performed in the APTAC adiabatic calorimeter operating at isothermal mode.

For the APTAC measurements, dilute aqueous solutions of hydroxylamine (HA),  $\text{NH}_2\text{OH}$ , and hydroxylamine nitrate (HAN),  $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ , were kept at constant temperature for different lengths of time, and the liquid-phase products were subsequently analysed with HPLC, IC, and UV. In measurements employing the SIMULAR calorimeter, aliquots were withdrawn from the reactor during the reaction and were also analysed by HPLC, IC, and UV. Hydroxylamine was supplied by Fluka in a 50% aqueous solution (55458 purum, ~50% in  $\text{H}_2\text{O}$ ) and was used without any further purification. Hydroxylamine nitrate was also supplied by Fluka in an 18% aqueous solution (93726 purum, ~82% in  $\text{H}_2\text{O}$ ) and was also used without any further purification. Milli-q water was used for all dilutions.

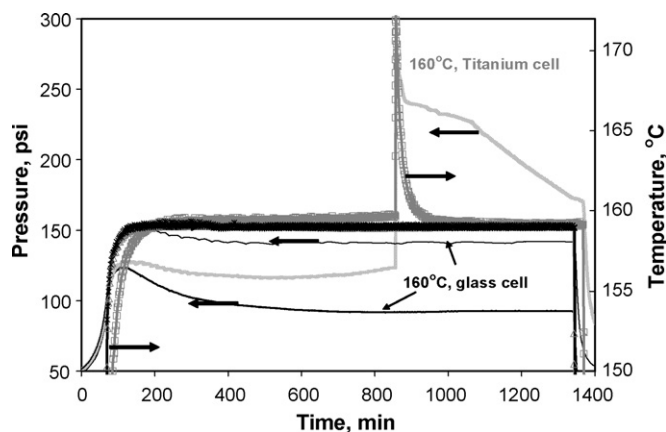
## 3. Results and discussion

Isothermal experiments were performed using aqueous solutions of hydroxylamine and hydroxylamine nitrate in open and closed systems in the temperature range 80–160 °C.

### 3.1. APTAC and analytical measurements

Hydroxylamine experiments were performed isothermally in a closed glass cell in APTAC at 130, 140, and 150 °C and in a closed titanium cell at 130 °C. The pressure and temperature history of typical measurements are displayed in Fig. 1.

As can be seen in Fig. 1, there is no evidence of HA decomposition in a glass cell at 130 °C during the 1200 min of the measurement. At 140 °C a measurable rate of decomposition starts at approximately

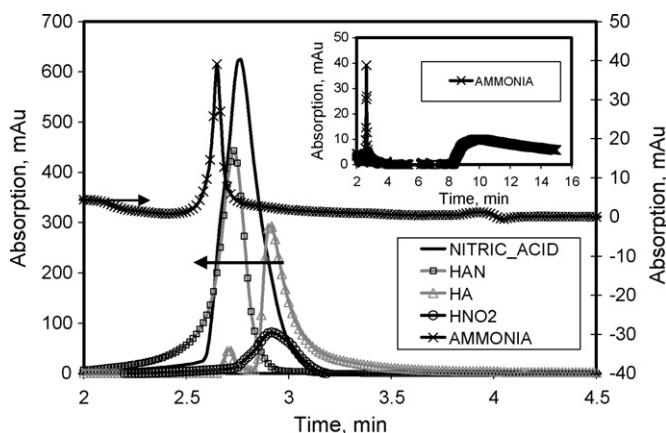


**Fig. 2.** Pressure and temperature history of HAN decomposition in titanium and glass cells at 160 °C. Plain lines show pressure variation, and lines with markers show temperature variation. Black colour is used for glass-cell measurement and grey for the titanium-cell one.

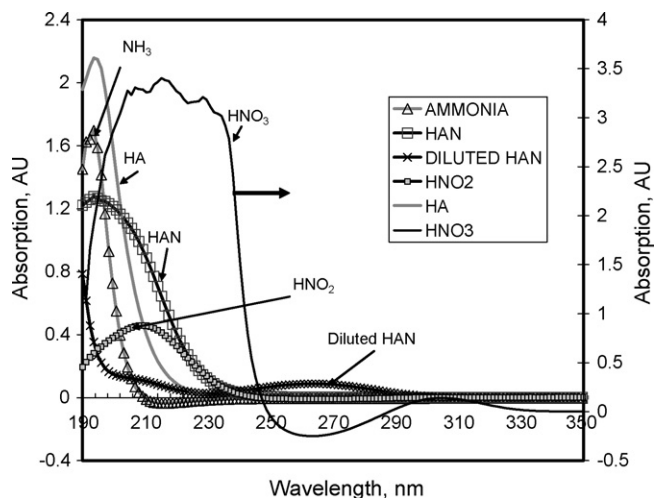
300 min, while both pressure and temperature profiles develop smoothly. At 150 °C, decomposition starts faster. The decomposition induces a steep pressure rise of ~60 psi, which results in immediate reactor venting. Finally, the HA decomposition reaction in the titanium cell develops as the cell is heated to reach the desired temperature of isothermal operation, 130 °C and its very rapid pressure rise activates the pressure relief system.

Similar isothermal measurements were performed employing HAN, in a closed glass cell in the APTAC at 100, 120, 130, 140, 150 and 160 °C and in a closed titanium cell at 160 °C. As can be seen in Fig. 2, no evidence of HAN decomposition was observed at any temperature in the glass cells for the duration of the measurement, a period of approximately 1400 min. However, after approximately 800 min at 160 °C the substrate in the titanium cell reacted in a very violent autocatalytic form to raise the pressure and the temperature of the system vertically.

To elucidate the behavior of the reacting system prior to its run-away, a series of measurements were performed in the APTAC at 100 °C employing ~6 g of 18% HAN aqueous solution in closed glass cells. The final products of those experiments, which had a different duration, were analysed by means of HPLC, IC, and occasionally UV. HPLC and UV absorption data of HA and HAN standards are shown in Figs. 3 and 4.



**Fig. 3.** HPLC analyses of HA, HAN,  $\text{HNO}_3$ ,  $\text{HNO}_2$  (all read on the left-hand ordinate) and ammonia (read on the right-hand ordinate). The absorption of ammonia at longer times is also shown in the embedded figure.

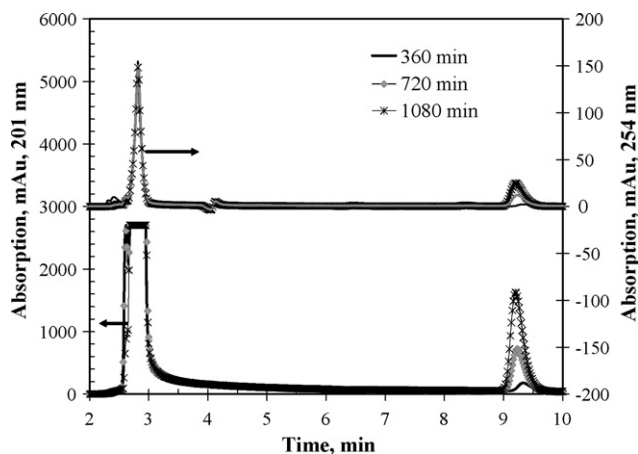


**Fig. 4.** UV spectra of ammonia, HNO<sub>3</sub>, HNO<sub>2</sub>, HA, and HAN. HAN spectra is shown under two, significantly different, dilutions. HNO<sub>3</sub> spectrum is read on the right-hand ordinate. All other substances absorption is read on the left-hand ordinate.

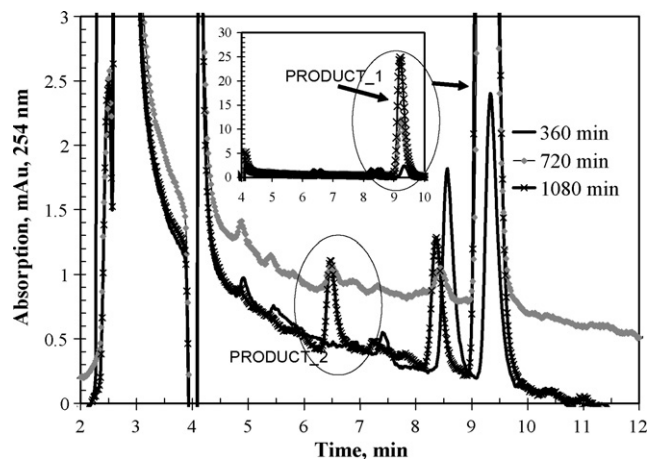
Typical HPLC measurements with the solution absorption spectra at 201 and 254 nm are shown in Figs. 5–11, while a typical IC measurement is shown later in Fig. 13.

Ammonia, nitrites and nitrates are typical products of HA and HAN decompositions, thus their absorption spectra were considered here. As can be seen in Fig. 3, HA, HAN ammonia, nitrates and nitrites have a retention time near 2.8 min, so quantification of the unreacted HAN cannot be performed solely via this type of HPLC analysis. The exact form of the very broad peak that ammonia demonstrates after 8 min depends on dilution and pH. On the other hand, as shown in Fig. 4, HA, and ammonia have a similar UV absorbance spectrum, while the UV absorbance spectrum of HAN is affected by dilution.

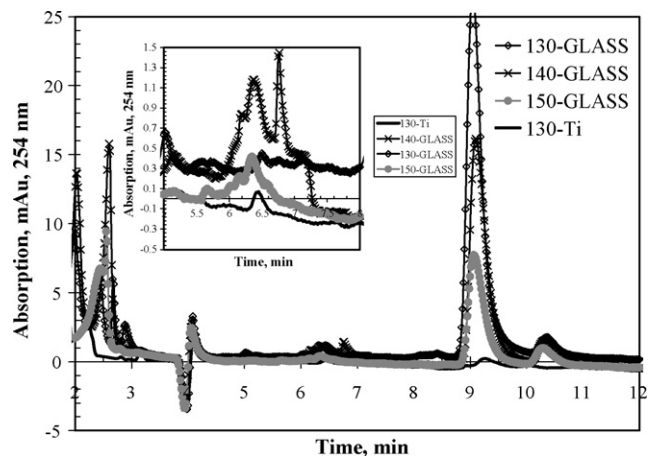
The HPLC analysis of the *undiluted* final products of three measurements employing HAN aqueous solutions in a glass cell, performed at 100 °C and at the same conditions but different measurement durations, are shown in Fig. 5. No heat release or pressure rise was measured during the duration of the respective measurements. As can be seen in Fig. 5, even at the shortest experiment and in spite of the low temperature, a product with retention time 9.3 min is formed. This product subsequently decomposes further as is shown later. A similar product with retention time 9.3 min, is



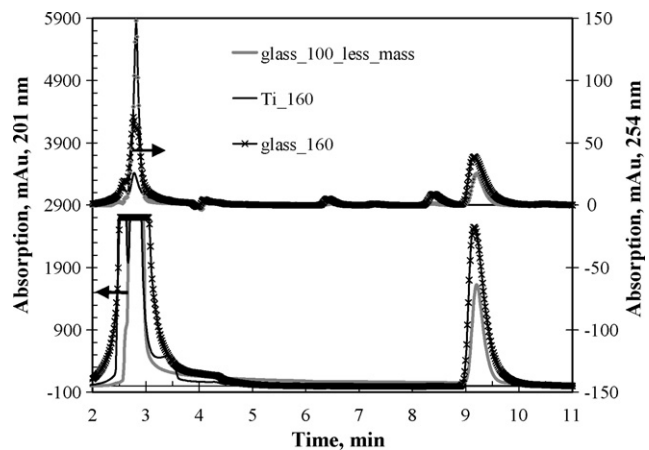
**Fig. 5.** HPLC measurement and absorption at 201 and 254 nm for HAN decomposition solutions. HA, HAN and nitrates absorb at 2.9 nm. Unidentified product peak is at retention time 9.3 min.



**Fig. 6.** HPLC measurement and absorption at 254 nm for HAN decomposition product solutions. The unidentified product with retention time 9.3 min (product 1) and product with retention time 6.5 min (product 2) are shown inside the circles.



**Fig. 7.** HPLC measurement and absorption at 254 nm for HA decomposition solutions. Unidentified products with retention times 9.3 and 6.5 min are shown.



**Fig. 8.** HPLC measurement and absorption at 201 and 254 nm for HAN decomposition solutions at 160 °C in a glass and a titanium cell and at 100 °C in a glass cell. The measurement at 100 °C employed less mass of reactant than for the other two measurements.

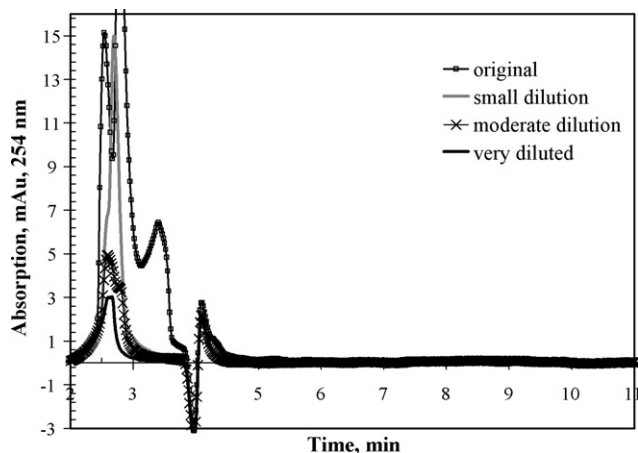


Fig. 9. HPLC analysis of the HAN measurement in a Ti cell at 160 °C.

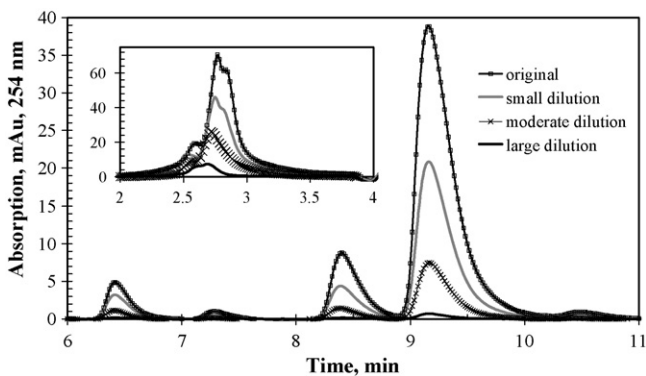


Fig. 10. HPLC analysis of the HAN measurement in a glass cell at 160 °C.

obtained during the HA decomposition. At 201 nm analysis wavelength, a broad peak also appears between 5 and 10 min in both HAN and HA decomposition samples.

Fig. 6 shows the chromatogram of the measurement shown in Fig. 5 at 254 nm, in a different scale. As can be seen in Figs. 4 and 5, the original reactants do not absorb significantly at wavelengths greater than 230 nm (150 mAu at 254 nm vs. well over 3000 mAu at 201 nm for the original reactant and 2500 mAu vs. 50 mAu for product with retention time 9.3 min, as can be seen in Fig. 6). Nevertheless, at the concentrations of these samples,

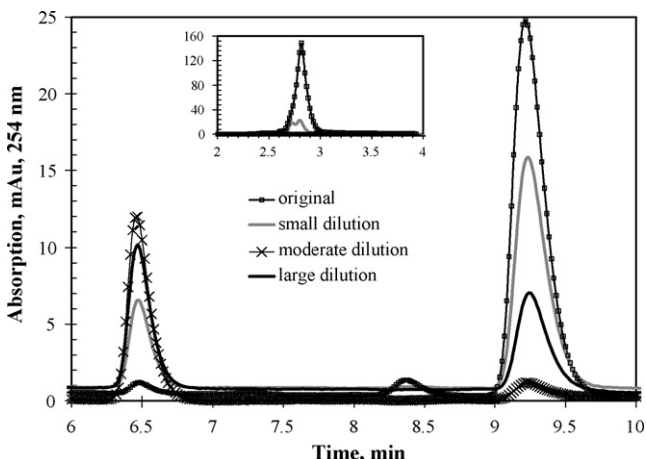


Fig. 11. HPLC analysis of the HAN measurement in a glass cell at 100 °C.

their absorption is not negligible and can be used for quantitative comparisons.

Fig. 6 shows the same set of data as displayed in Fig. 5 at 254 nm but in a different scale. As can be seen in Fig. 6 at 6.4 min, a second product peak appears. The highest peak of product 2 corresponds to the longest measurement, while it has not made its appearance in the shortest one. The product 2 area for the middle duration measurement is between the other two. The same product appears during the HA decomposition, as shown in Fig. 7.

Based on some evidence discussed later, it is believed that both products 1 and 2, i.e., the unidentified compounds with retention times 9.3 and 6.4 min, respectively, are ammonia-related compounds.

Fig. 7 shows the analysis of the end products of four HA thermal decomposition measurements performed at different temperatures and presented earlier in Fig. 1. As can be seen in Fig. 7, the highest peak of product 2 corresponds to the measurement at 140 °C, where, as shown in Fig. 1, decomposition of HA has occurred but not sufficiently violently to vent the reactor. Measurements at 150 °C in glass and 130 °C in titanium resulted in a rapid pressure rise and reactor venting. As can be seen in Fig. 7, no measurable quantity of product 2 is shown in the measurement in glass at 130 °C, where product 1 concentration is the highest. This may indicate that product 2 is a product formed in a subsequent reaction stage, probably from the decomposition of product 1. On the other hand, it is also possible that product 2 corresponds to a volatile compound that can be directly or indirectly affected by ventilation (and ammonia is one of those), thus, in this particular case, its concentration in the solution would have been inevitably affected by the venting of the reacting cell.

Additional experimental measurements, not shown here, have given further evidence to the first assumption (product 2 is formed in a second stage, from the decomposition of product 1). Moreover, it is plausible that the reaction runaway is triggered by the product 2 compound.

Fig. 8 shows curves obtained from *undiluted* HAN decomposition samples. Two of the measurements were performed under very similar conditions (160 °C, 1400 min experiment duration, ~10 g of 18% HAN diluted in 20 g of water). The temperature and pressure history of these two reactions for the 1400 min that the samples were left to react, prior to being analysed, were shown in Fig. 2. The third measurement was performed at 100 °C, with the isothermal operation maintained for 1080 min, employing ~5 g of 18% HAN. As can be seen in Fig. 8, in the measurement employing the Ti cell no product with retention time (RT) 9.3 min appears at either wavelength, while it is inconclusive, as explained earlier, if the first peak corresponds to unreacted HAN, HA, or their products of decomposition. In any case, the measurement employing the titanium cell displays a multiple peak at 254 nm and RT ~2.9 min indicating the existence of at least two compounds, and its size is the smallest of the three measurements shown here. Similarly, no product with RT 6.4 min was found from the measurement in the Ti cell, which was also vented due to its rapid runaway reaction.

Also shown in Fig. 8, the measurement at 160 °C employing the glass cell has a larger potentially unreacted HAN concentration, some product with RT 9.3 min and the highest product 2 (RT 6.4 min) concentration. Finally, the measurement in the glass cell at 100 °C has the highest peak of the potentially unreacted HAN, some product 1 (RT 9.3 min) and also some product 2 (RT 6.4), which is not shown clearly at this scale. Both, products 1 and 2 concentrations are lower in this measurement than in the measurement in the glass cell at 160 °C. However it is noted that up to this conversion level, no measurable heat generation (which would have been expressed as a temperature rise) or gas generation (pressure



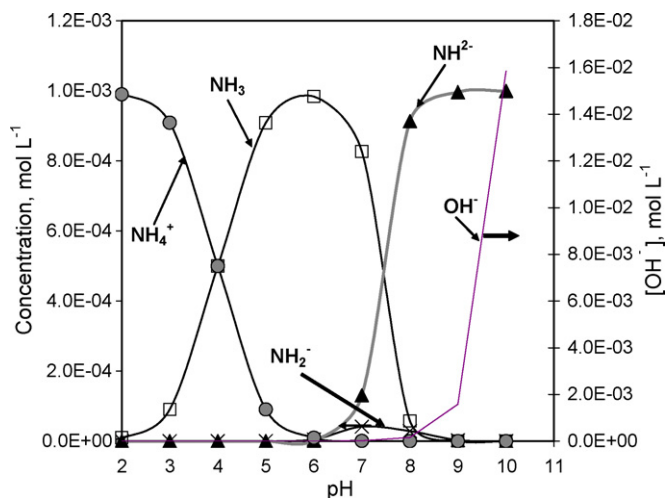


Fig. 12. Dissociation of ammonia in aqueous solutions as a function of pH [6].

rise) was observed for these two measurements, as shown in Fig. 2.

In order to perform quantitative comparisons of the potentially unreacted HAN masses of the three measurements shown in Fig. 8, the samples were diluted. Although dilution did not have an effect on measurements at 160 °C, as shown in Figs. 9 and 10, it did have a significant effect on the measurement performed at 100 °C, as shown in Fig. 11.

Fig. 9 shows the absorption spectra at 254 nm of the product obtained from the measurement performed at 160 °C in the titanium cell at different dilutions. As can be seen in this figure, neither product 1 or product 2 or any other product appears. Dilution affects the height of the peak at 2.9 min as well as its shape, but as reported earlier useful information cannot be extracted from this peak. The same observations were made at all tested wavelengths.

Fig. 10 shows the absorption spectra at 254 nm of the product obtained from the measurement performed at 160 °C in the glass cell at different dilutions. As can be seen in this figure, both products 1 and 2 are present in the sample, while more peaks have appeared at 8.4 and 7.3 min. Dilution slightly affects the shape of the peak at 2.9 min and results in a proportional reduction of the size of each one of the peaks shown here. The same observations were made at all tested wavelengths.

Fig. 11 shows the absorption spectra at 254 nm of the product obtained from the measurement performed at 100 °C in the glass cell employing less reactant, at different dilutions. As can be seen in this figure, both products 1 and 2 are present in the sample. A peak has also appeared at 8.4 min but no peak is detected at 7.3 min. However, in this case dilution has resulted in an inversely proportional change in the size of peak of product 2. So, as dilution increases, its size also increases. This is potentially done at the expense of one of the substances with RT 2.9 min. This assumption is based on the observation that this peak has disappeared in the final two dilutions and reduces with dilution disproportionately when compared with the respective peak reduction of the sample at 160 °C, Fig. 10 (dilution was the same in both cases).

The UV spectrum of product 2 – substance with retention time 6.4 min – expands from 220 to 320 nm with a peak at 266 nm as can be later seen in Fig. 14.

Although the UV spectrum of diluted HAN displays absorbance in the same range as can be seen in Fig. 4, from surrogate solutions containing ammonia, nitrates, and nitrites (compounds involved in the course of decomposition of HA and HAN [5]) the analysis of only ammonia solutions at pH greater than 8 exhibited peaks of

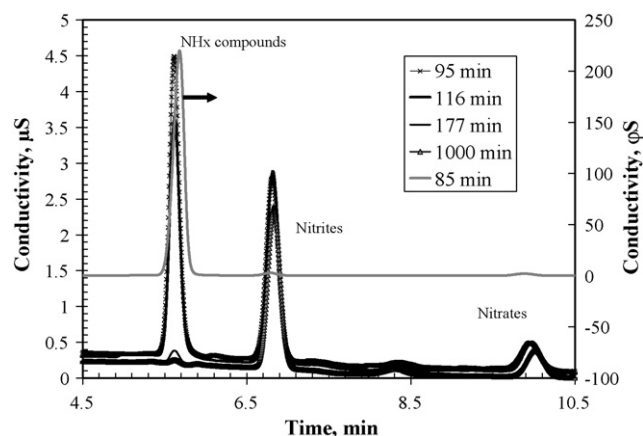


Fig. 13. IC analytical results from the isothermal HA decomposition in an open system with reflux at 353 K.

similar retention time and UV spectrum in samples in a systematic way.

Fig. 12 provides the dissociation of  $\text{NH}_3$  in aqueous solutions as a function of pH. Calculations of the concentrations of different ions were based on the data provided by Stumm and Morgan [6]. Although the nature of this compound with RT 6.4 min has not been fully identified so far, it has been encountered in a number of samples that had a pH in the range of 9–12. In view of the data of Fig. 12, it is believed that it is most likely  $\text{NH}_2^-$ . In other words, it is postulated that HA and HAN decompose to form ammonia, which is then dissociated to  $\text{NH}_2^-$  and subsequently to nitrates, nitrites, and/or other compounds.

The decomposition of aqueous solutions of HAN (which have a low, acidic pH) starts at much higher temperatures, which is consistent with the assumption of ammonia formation, the increase in pH that it induces so as to result in  $\text{NH}_2^-$  formation, and its subsequent runaway. And although there is not sufficient evidence to substantiate such an argument, the findings of Wei [7] are consistent with this assumption. More specifically, Wei, 2005, found that an earlier onset of HA decomposition is observed and a larger amount of heat is generated when sufficiently high concentrations of KOH are added to the HA aqueous solution. Thus, it is not unlikely that this compound, which is produced by  $\text{NH}_3$  dissociation, appears at higher pH and triggers the reaction runaway.

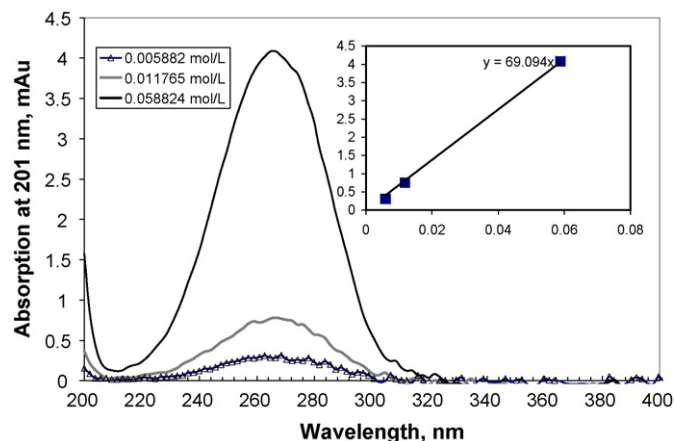


Fig. 14. Absorption spectrum of unidentified compound with retention time 6.4 min obtained for three different ammonia model solutions at pH above 10.

### 3.2. Heat-flow isothermal calorimetry measurements

Preliminary HA in aqueous solution decomposition runs were also performed in a modified SIMULAR heat-flow calorimeter in an open mode at 80 °C and in a closed high pressure gas reactor in the range 100–130 °C. Aliquots withdrawn during the reaction were analysed via HPLC and IC chromatography. After 8–20 h of operation at isothermal conditions, some conversion of the original substrate was achieved but no measurable heat generation was produced except in the measurement at 130 °C.

A few hours after the initiation of the measurement, IC data stopped showing any measurable variation in the concentrations of nitrate and nitrite ions, as shown in Fig. 13. As visible in Fig. 13, at the early stages of the reaction formation of what is identified as an ammonia-related compound (most likely  $\text{NH}_2^-$  or possibly  $\text{NH}_2^-$ ) predominates, and this compound subsequently gives way to the formation of nitrates and nitrites. There is evidence that the product with IC retention time 5.6 min is related to the product with HPLC retention time 6.4 min and corresponds to an ammonia-related compound, possibly  $\text{NH}_2^-$  or  $\text{NH}_2^-$ .

$\text{NH}_3$  standards with a pH in the range of 11–12 were analysed by IC, and a single peak appeared at 5.6 min. Moreover, aqueous solutions of  $\text{NH}_3$  in the same pH range and at different dilutions resulted in an HPLC peak at 6.4 min. Moreover its peak height was linearly related to the  $\text{NH}_3$  concentration in the solution, as can be seen in Fig. 14. Further research is currently underway.

### 4. Conclusions

Isothermal decomposition tests were performed on HA and HAN aqueous solutions in the temperature range 80–160 °C. Products were analysed by HPLC, ion chromatography, and UV. Condition-dependent autocatalytic decompositions were demonstrated for HA and HAN, and an intermediate product was observed that is likely to be responsible for the observed autocatalytic behavior. This product is most likely an ammonia-related compound, such as  $\text{NH}_2^-$  or  $\text{NH}_2^-$ . Further experimental work is currently underway targeting firstly the complete identification of products and stable radicals produced during the decomposition and subsequently the measurement of the heat of reaction during isothermal decomposition.

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