

Thermal runaway reaction hazards and mechanisms of hydroxylamine with acid/base contaminants

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Abstract

Hydroxylamine (HA) has been involved in two incidents since 1999 because of its thermal instability and incompatibility. In this study, thermal runaway reactions of hydroxylamine with various concentrations of KOH and HCl were studied using the reactive system screening tool (RSST) and automatic pressure tracking adiabatic calorimeter (APTAC). The thermokinetic data, such as onset temperature, heat of reaction, maximum self-heat rate, maximum pressure rate, and non-condensable gas pressure, were compared with those of hydroxylamine solution without added impurity. Our study shows that the thermal decomposition behavior of hydroxylamine is affected by the presence of acid/base, and mixing of hydroxylamine with acid/base may cause thermal decomposition at lower temperatures. Different decomposition pathways can be initiated by hydrogen ion and hydroxide ion. The decomposition mechanisms of hydroxylamine in alkaline and acidic solutions are proposed based on the products, information from the literature, and quantum mechanical calculations. The experimental results are discussed in terms of the proposed reaction mechanisms.

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1. Introduction

The effect of contamination is often considered as a cause of incidents in the chemical industry. The presence of trace impurities may reduce the thermal stability of a nominally pure chemical and cause unexpected runaway reactions under normal process conditions and they can explode and cause death and destruction of property [1]. Hydroxylamine (HA) has been involved in two tragic incidents since 1999 [2,3]. Because of the industrial importance of hydroxylamine [4] and relatively limited information about its thermal stability in the open literature, it is important to study potential reactive hazards under process conditions and provide guidelines for safety and control measures. The catalytic effect of metals and metal ions on the thermal decomposition of hydroxylamine was studied by Cisneros et al. [5] and Iwata et al. [6]. This paper presents the effect of acid/base contamination on the thermal runaway reaction of hydroxylamine using data from reactive system

screening tool (RSST) and automatic pressure tracking adiabatic calorimeter (APTAC). The onset temperature (T_0), maximum temperature (T_{\max}), adiabatic temperature rise ($\Delta T_{\text{adiabatic}}$), maximum pressure (P_{\max}), self-heat rate at onset temperature (dT/dt_0), maximum self-heat rate (dT/dt_{\max}), maximum pressure rate (dP/dt_{\max}), and non-condensable gas pressure were determined for runaway hazard evaluation.

Understanding the mechanism behind the runaway reaction is important for process safety because conditions can be identified that may favor or temper the occurrence of the runaway reaction. It can also provide a good model for scale-up of the experimental information. The final products of the reaction can be analyzed by various experimental techniques. Most of the intermediates and transition states are short lived and it is difficult to study them experimentally. Theoretical quantum mechanical calculation is a powerful tool to study the mechanism of runaway reactions. Based on the experimental runaway behavior, products, information from the literature and chemical intuition, the most likely reaction pathway can be identified with the assistance of quantum mechanical calculations. In this paper, frequency calculations were carried out on the optimized geometry of

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the reactants, the intermediates, and the products using hybrid density functional theory at the B3P86/cc-pVDZ [7,8] level of theory with Gaussian 98 suite of program [9]. The calculated enthalpies with zero-point energy correction were used to calculate the heats of reaction for every elementary step in the proposed reaction network.

2. Experimental

2.1. Materials

Standard hydrochloric acid solutions (Sigma, catalog numbers 35327 and 35328) and standard potassium hydroxide solutions (Aldrich, catalog numbers 31932 and 31937, Sigma, 17-8) were mixed with hydroxylamine solution (Aldrich, catalog number 45780, 99.999%, 50 mass% in water) to simulate acidic and basic contaminations, respectively. In order to maintain the same sample thermal inertia, the same amount of water (Aldrich, catalog number 32007, ACS reagent) was added to hydroxylamine solution to prepare 43 mass% hydroxylamine solutions to simulate thermal runaway conditions without contaminations. Potassium chloride solution (Fluka, catalog number 60142, 1 M in water) was also used to study the effects of potassium or chloride ions on the thermal runaway hazards. All of these chemicals were used without further purification and analysis.

2.2. Reactive system screening tool (RSST)

The RSST, manufactured by Fauske and associates, is a calorimeter for rapid measurements of reaction thermal behavior for temperatures up to 400 °C and pressures up to 3549 kPa. An open, 10 cm³ sample cell typically made of glass is placed inside a pressure vessel (400 cm³) which can withstand pressures up to 3549 kPa. The RSST can be used not only for screening the reactive chemicals, but also for designing emergency relief devices. Detailed descriptions of the RSST can be found in references [10,11]. The RSST is a pseudo-adiabatic calorimeter and it attempts to compensate heat losses by adding additional energy determined by calibration of the heater. The heating rate can be varied from 0.25 °C/min up to the rates required to simulate fire or explosion. In this paper, glass thermocouples and polymer coated magnetic stirrer bars were used to provide a neutral environment for the reactions. A fixed heating rate of 1 °C/min was used for the temperatures up to 400 °C. The shut-down pressure limit was 3204 kPa. Initial nitrogen pressures of 1480–1825 kPa were used to minimize material loss from the sample cell.

2.3. Automatic pressure tracking adiabatic calorimeter (APTAC)

Adiabatic calorimeter 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 as close as possible to the temperature of the sample. Following the screening RSST tests, measurements were made with an APTACTM developed by TIAX LLC [12]. The APTAC calorimeter can be operated in a variety of test modes, such as heat-wait-search, heat ramps, and isothermal aging with temperatures up to 500 °C and pressures ranging from vacuum to 13 790 kPa. It can track exotherms at heat generation rates from 0.04 to 400 °C/min. It can produce low thermal inertia data because 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. For the present work, the measurements were conducted in glass sample cells of nominal 100 cm³, which can provide a neutral environment for the reactions. Teflon coated thermocouples were used to prevent the contact of hydroxylamine solution with metals.

APTAC heat-wait-search mode was used: the sample was heated at 2 °C/min to a starting temperature, and the temperature was allowed to stabilize for 20 min. Then the APTAC continued at that temperature and started searching for exothermic behavior. During the search period, the temperature of the containment vessel gas was adjusted to match that of the sample. If the self-heat rate of the sample was greater than a preset threshold (0.1 °C/min), the apparatus tracked the reaction adiabatically until the reaction ended or one of the shut-down criteria was met. If no exotherm was detected, the apparatus would heat the sample to the next search temperature and the steps repeated until one of the shut-down criteria was met. The onset temperature is defined as the temperature when an exotherm is detected and it is usually the lowest temperature when the sample self-heat rate surpasses the preset threshold in the ‘search’ or ‘adiabatic’ mode.

A summary of APTAC test setup conditions can be found in the Table 1. Due to the high exothermic reactivity of hydroxylamine solution, only small sample sizes (about 4 g) were used in these tests, so stirring was not necessary. To prevent undesired contaminations, the tubing lines between sample cell and transducers and also the tubing leading to valve 1 were flushed with acetone following every experiment. The tubing was allowed to dry by flushing with compressed nitrogen.

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 even more difficult to estimate the heat of the reaction from the experiment. The liquid heat capacity of hydroxylamine is missing in the literature, but the heat capacities in gas and solid phases are very close to those of water. Because water was the solvent and a major product in this experiment, the liquid heat capacity of water (4.18 J/g/°C) was used to

Table 1
Summary of the APTAC experimental setup conditions

Thermocouple	Teflon coated
Heat mode	H–W–S
Start temperature (°C)	50
Limit temperature (°C)	180
Temperature increment (°C)	10
Cool down temperature (°C)	50
Exotherm threshold (°C)	0.1
Heat rate (°C/min)	2
Stirring	NO
Venting	NO
Injection	NO
Shut down criteria	
Temperature level (°C)	300
Heat rate (°C/min)	400
Pressure imbalance (kPa)	1034
Minimum pressure (kPa)	138
Over pressure (kPa)	7
Lower band (kPa)	–70
Upper band (kPa)	70
Exotherm limit (°C)	300
Pressure level (kPa)	8.273
Pressure rate (kPa/min)	13.790

estimate the thermal inertia [13] ($\phi = mC_v / (mC_v + m_b C_{vb})$) and the heat of reaction from the APTAC experimental results.

3. Results and discussions

3.1. Potassium hydroxide (KOH)

Potassium hydroxide is a strong base, alkaline in solution, highly corrosive, and incompatible with high concentration acids. The chemical reactivity Worksheet from the National Oceanic and Atmospheric Administration (NOAA) [14] shows no reaction between KOH and hydroxylamine if they are to be mixed. When a catastrophic hydroxylamine explosion occurred on 19 February 1999, at the Concept Sciences, Inc., potassium hydroxide was being used to react with hydroxylamine sulfate in the hydroxylamine production processes. To the best of our knowledge, there is little information on the thermal stability of hydroxylamine with alkaline contaminants in the literature.

Various concentrations of KOH solutions were used to mix with 50 mass% hydroxylamine solution. The experimental conditions and results of the RSST and the APTAC tests are listed in Tables 2 and 3, respectively. Each sample was tested three times to establish reproducibility and develop an estimate of the uncertainty. The apparent activation energies were calculated by Superchems Software, assuming first order reaction. As seen from Table 2 and Fig. 1, the onset temperature decreases significantly with increasing concentrations of KOH. Compared to hydroxylamine decomposition in water, additional heat was detected by the RSST for mixtures of hydroxylamine with KOH. High concentration KOH can also decrease the apparent activation energies of thermal decomposition. Onset temperature was below 50 °C for sample 7 with the highest concentration of KOH demonstrating that it is extremely hazardous to mix high concentration KOH with hydroxylamine solution. From a comparison of samples 4 with 7, the onset temperature is more sensitive to the concentration of KOH than the concentration of hydroxylamine. However, this cannot be applied to low concentration KOH conditions (samples 2, 3, 5, and 6).

Low concentration KOH conditions were tested in the closed cells of the APTAC. It is not uncommon to encounter contaminant concentrations from 0.1 to 2 mass% in process and storage conditions. Another reason is the corrosive nature of KOH. White residue was observed in the glass sample cells because SiO₂ was dissolved in the basic media at high temperatures. The APTAC results are presented in Table 3 and Figs. 2–5. In all of these tests, the liquid products were colorless and weighed about 3 g. 0.1N and 1N KOH solutions were added to 50 mass% hydroxylamine/water. The concentration of hydroxylamine in all the resulting HA/KOH mixtures is 43 mass%. The resulting concentrations of KOH are 0.15 and 1.5 mass%, respectively. The decomposition behavior of the 0.15 mass% KOH mixture is very close to that of hydroxylamine without KOH. The maximum heat and pressure rates are very close for the three samples, as shown in Figs. 3 and 5. For mixture of 1.5 mass% KOH, the onset temperature decreases by approximately 11 °C, and 18% more heat is released compared to those of hydroxylamine without KOH. Additionally, the maximum pressure is increased and also increased is the non-condensable gas pressure at 50 °C. The findings reveal that the decomposition

Table 2
Experimental results of the RSST tests

Samples	Mass concentration		Onset temperature (°C)	Maximum temperature (°C)	E_a (kJ/mol)
	HA (%)	KOH (%)			
(1) 6 ml 50 mass% HA/H ₂ O	50	0	139 ± 4	218 ± 2	160.7 ± 14.6
(2) 6 ml 50 mass% HA/H ₂ O + 1 ml 0.1N KOH	43	0.15	134 ± 4	212 ± 2	122.6 ± 2.1
(3) 6 ml 50 mass% HA/H ₂ O + 1 ml 1N KOH	43	1.5	114 ± 4	214 ± 2	114.6 ± 19.2
(4) 6 ml 50 mass% HA/H ₂ O + 1 ml 8N KOH	43	12	86 ± 2	246 ± 6	92.5 ± 7.9
(5) 6 ml 50 mass% HA/H ₂ O + 2 ml 0.1N KOH	38.5	0.17	125 ± 5	209 ± 1	123.8 ± 7.1
(6) 6 ml 50 mass% HA/H ₂ O + 2 ml 1N KOH	38.5	1.7	112 ± 4	215 ± 2	100.8 ± 5.4
(7) 6 ml 50 mass% HA/H ₂ O + 2 ml 8N KOH	38.5	13.6	46 ± 2	246 ± 8	74.1 ± 0.4

Table 3
APTAC experimental results of the KOH effect on the thermal decomposition of hydroxylamine

Samples	HA (3 ml)	KOH (0.5 ml)	T_0 (°C)	T_{max} (°C)	P_{max} (kPa)	dT/dt_0 (°C/min)	dT/dt_{max} (°C/min)	dP/dt_{max} (kPa/min)	Non-condensable (kPa (50 °C))	ΔH_{rxn} (kJ/mol)
HA + water	43 mass%	0	123.4 ± 0.6	236.7 ± 3	4157 ± 214	0.14 ± 0.04	38 ± 3	1910 ± 148	414 ± 7	113.8 ± 2.5
HA +0.1N KOH	43 mass%	0.15 mass%	122.6 ± 0.3	234 ± 0.5	3993 ± 148	0.11 ± 0.01	24 ± 3	1262 ± 152	414 ± 14	114.2 ± 0.8
HA +1N KOH	43 mass%	1.5 mass%	112.7 ± 0.8	244.7 ± 2	4909 ± 207	0.17 ± 0.07	34 ± 4	1510 ± 110	579 ± 34	134.3 ± 2.9

Note: Phi factor=3.25, assuming constant sample $C_p = 4.18 \text{ J/g/K}$.

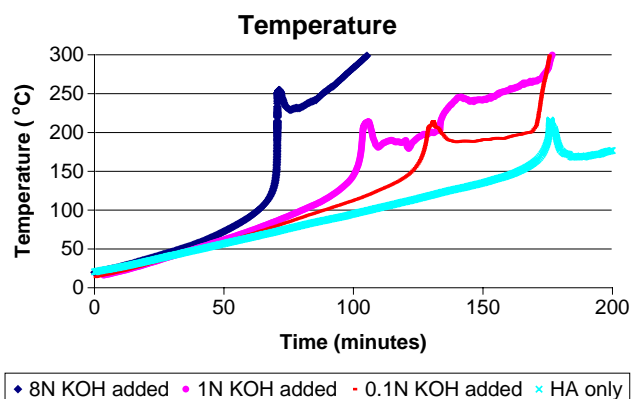


Fig. 1. RSST results of thermal decomposition of 6 ml 50 mass% HA/H₂O with 1 ml various concentrations of KOH.

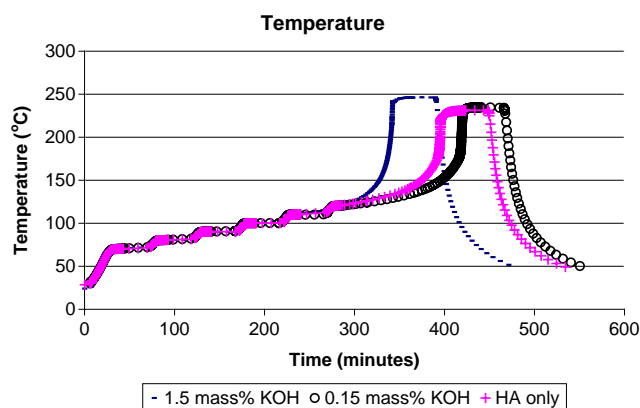


Fig. 2. APTAC results of temperature for thermal decomposition of HA with KOH.

pathway initiated by KOH or the ratio of the decomposition products is different from the hydroxylamine decomposition without impurities. Further investigation is needed to resolve this issue and determine the reaction mechanism.

3.2. Hydrochloric acid (HCl)

As shown in the previous section, the thermal decomposition of hydroxylamine is accelerated by KOH. In order

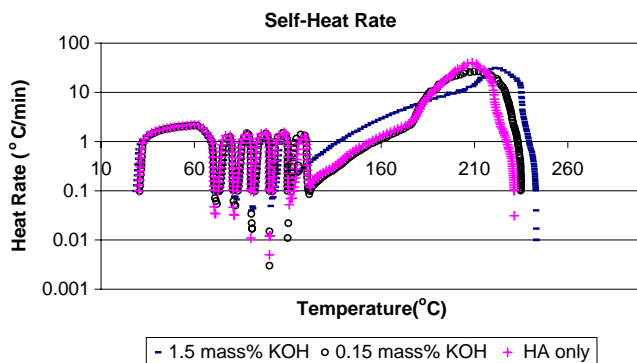


Fig. 3. APTAC results of self-heat rate for thermal decomposition of HA with KOH.

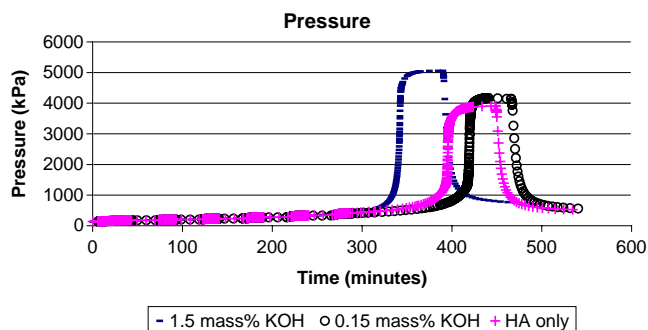


Fig. 4. APTAC results of pressure for thermal decomposition of HA with KOH.

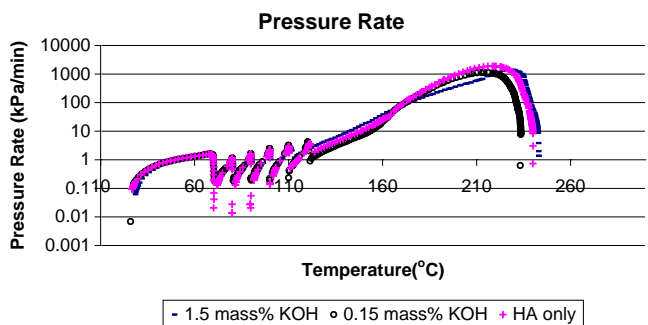


Fig. 5. APTAC results of pressure rate for thermal decomposition of HA with KOH.

to test the effect of acidic impurity on the thermal decomposition of hydroxylamine, 1N and 2N hydrochloric acid solutions were added to 50 mass% hydroxylamine/H₂O solution and the concentrations of the acid impurity in the resulting mixtures are about 0.5 mass% and 1 mass%, respectively. The concentration of hydroxylamine in the resulting mixtures is 43 mass%. The experimental results from the APTAC are presented in Table 4 and Figs. 6–9. At the low concentration of 0.5 mass% HCl, the maximum pressure increases by 689 kPa and maximum temperature

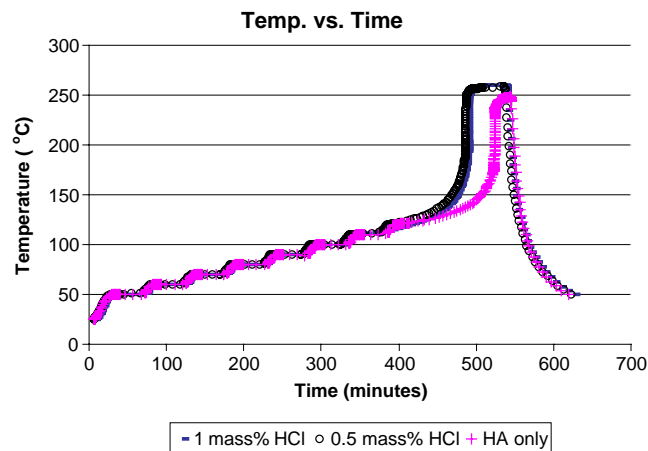


Fig. 6. APTAC results of temperature for thermal decomposition of HA with HCl.

Table 4

APTAC experimental results of the HCl effect on the thermal decomposition of hydroxylamine

Samples	HA (3 ml, mass%)	HCl (0.5 ml)	T ₀ (°C)	T _{max} (°C)	P _{max} (kPa)	dT/dt ₀ (°C/min)	dT/dt _{max} (°C/min)	dP/dt _{max} (kPa/min)	Non-condensable (kPa (50°C))	ΔH _{rxn} (kJ/mol)
HA + water	43	0	122.8 ± 0.7	246.5 ± 2	4750 ± 117	0.12 ± 0.01	69 ± 3	3585 ± 207	414 ± 7	116.7 ± 2.9
HA + 1N HCl	43	0.5	123.2 ± 0.6	257.2 ± 1	5530 ± 110	0.17 ± 0.04	95 ± 8	5695 ± 275	441 ± 14	123.0 ± 3.8
HA + 2N HCl	43	1	113.4 ± 0.5	257 ± 4	5340 ± 296	0.13 ± 0.04	95 ± 12	5667 ± 345	434 ± 7	136.0 ± 5.9

Note: Phi factor=2.9, assuming constant sample C_p = 4.18 J/g/K.

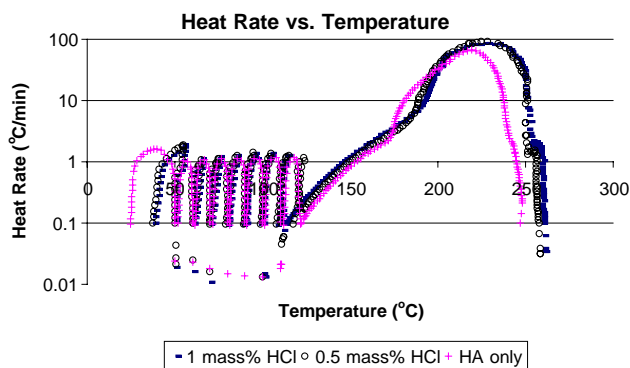


Fig. 7. APTAC results of self-heat rate for thermal decomposition of HA with HCl.

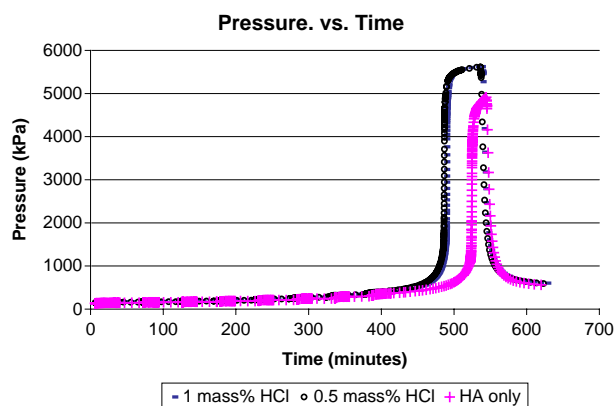


Fig. 8. APTAC results of pressure for thermal decomposition of HA with HCl.

by 10 °C. The maximum self-heat rate and pressure rate also increase significantly. The decomposition behavior of the mixtures with 0.5 mass% and 1 mass% HCl are very close except that the onset temperature of the 1 mass% HCl mixture is about 10 °C lower. The liquid products of these tests were clear and there was smell of ammonia. In addition, the non-condensable gas pressures for mixtures with acidic impurities are a little higher than those of hydroxylamine without HCl. Finally, the added 1 mass% HCl solutions caused 16% more heat release from the mixtures. From these re-

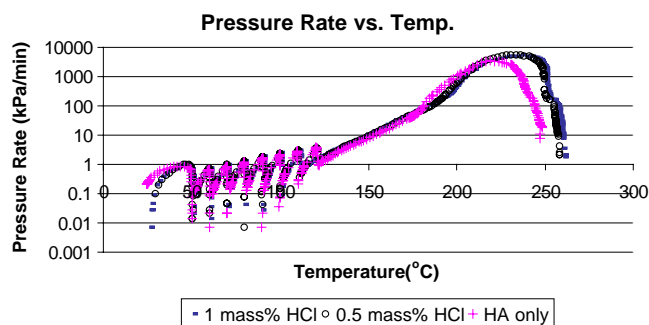


Fig. 9. APTAC results of pressure rate for thermal decomposition of HA with HCl.

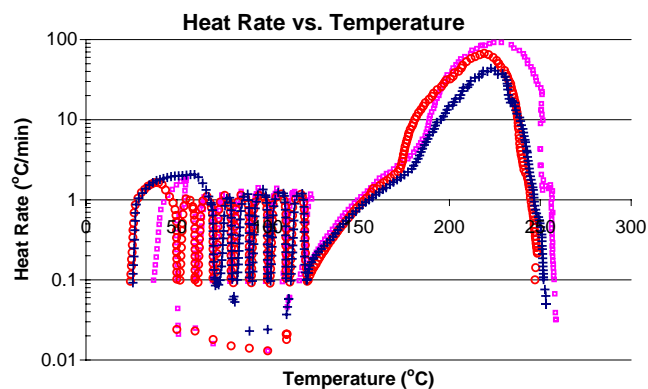


Fig. 10. Comparison of HCl and KCl on the self-heat rate of HA decomposition.

sults, we conclude that hydrochloric acid also can accelerate the thermal decomposition of hydroxylamine at the elevated temperatures and mixing of HCl and hydroxylamine should be avoided during process and storage conditions.

3.3. Potassium chloride (KCl)

As discussed above, both KOH and HCl can accelerate the thermal decomposition of hydroxylamine. The addition of 1N KOH solution decreases the onset temperature by 10 °C and the addition of 1N HCl solution increases the maximum self-heat rate and pressure rate. In order to verify that these changes in the hydroxylamine decomposition behavior were caused by hydroxide and hydrogen ions, mixture of 1 M KCl solution and hydroxylamine was tested with the APTAC. The summary of the results is listed in Tables 5 and 6. From Table 5, the onset temperature does not decrease after the addition of KCl solution, the maximum self-heat and pressure rates become lower, but the maximum temperature, maximum pressure, and non-condensable gas pressure increase. As shown in Table 6 and Figs. 10 and 11,

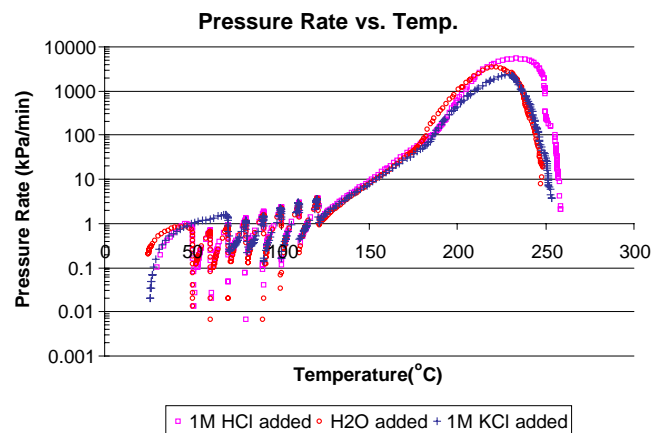


Fig. 11. Comparison of HCl and KCl on the pressure rate of HA decomposition.

Table 5
APTAC Experimental results of KCl effect on the thermal decomposition of hydroxylamine

Sample		Average T_0 (°C)	Average T_{max} (°C)	Average $\Delta T_{adabatic}$ (°C)	Average P_{max} (kPa)	Average dT/dt_{max} (°C/min)	Average dP/dt_{max} (kPa/min)	Average non-condensable (kPa (50 °C))
2.3 ^a	0 ^b	124.7	216	92	2992	21	1.006	296
2.3 ^a	0.34 ^a	125	230	105	3585	10	496	317

Note: Phi factor is about 5, assuming constant sample $C_p = 4.18$ J/g/K.

^a 50 mass% HA/H₂O (g).

^b KCl (1M) (g).

Table 6
Comparison of the decomposition of hydroxylamine with the addition of HCl, KCl, and H₂O

Sample		Average T_0 (°C)	Average T_{max} (°C)	Average $\Delta T_{adabatic}$ (°C)	Average P_{max} (kPa)	Average dT/dt_{max} (°C/min)	Average dP/dt_{max} (kPa/min)	Average non-condensable (kPa (50 °C))	Average ΔH_{rxn} (kJ/mol)
50 mass% HA/H ₂ O ^a	1 M HCl ^b	123.2	257.2	129	5530	95	5695	441	123.0
50 mass% HA/H ₂ O ^a	1 M KCl ^b	121.8	253	128	5171	44	2344	434	122.6
50 mass% HA/H ₂ O ^a	H ₂ O ^b	122.8	246.5	122	4750	69	3585	420	116.7

^a 3 ml.

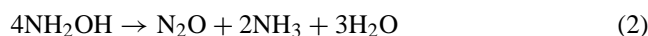
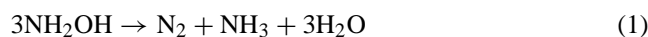
^b 0.5 ml.

the decomposition characteristics following the addition of KCl are very close to that of HCl except for the maximum self-heat rate and maximum pressure rate. It is most likely that potassium ion does not catalyze the decomposition of hydroxylamine. Chloride ion may participate in the decomposition and it may be oxidized by hydroxylamine, which caused more heat release. Based on the comparison, we can conclude that hydroxide ion caused a decrease in the onset temperature and hydrogen ion caused an increase in the maximum self-heat and pressure rates.

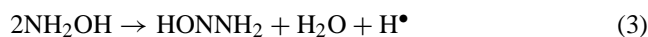
4. Proposed decomposition mechanisms under acidic and alkaline conditions

4.1. Decomposition products under acidic and alkaline conditions

In the literature, the decomposition of hydroxylamine has been described by a few mechanisms. Most of the proposed mechanisms are controversial and especially the intermediates of the decomposition are still in debate [15]. The decomposition of hydroxylamine is known to depend on the pH of the solution [4]. The pH of 50 mass% hydroxylamine/water solution is 10.6. Hydroxylamine free base decomposes at high temperatures according to Eqs. (1) and (2) with the ratio of 5/7 and 2/7, respectively [16]. The addition of base suppresses Reaction (2) in favor of Reaction (1), but the addition of acid causes the reverse effect and Reaction (2) became dominant [16].



The initiation reaction in both cases was proposed to be the formation of hydroxyhydrazine (HONNH₂):



This reaction is catalyzed by alkaline conditions and inhibited by acidic conditions. It followed that hydroxylamine was more stable in acidic than in alkaline solutions [4].

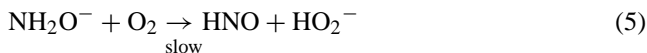
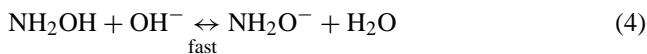
Our results show that hydroxylamine is not stable in acid solution and the maximum self-heat and pressure rates are higher than those in alkaline solution. Therefore, the initiation reactions and the decomposition mechanism must be different for the two conditions.

Under runaway conditions, the products of the thermal decomposition of 50 mass% hydroxylamine were reported as NH₃, H₂O, N₂, N₂O, and a small amount of NO and H₂ by Cisneros et al. [17]. The ratio of N₂ to N₂O was 2.9 in reference [17] which was close to 2.5 in reference [16]. NO and H₂ were also detected because a wide spectrum of reactions can be initiated at high temperatures and in a closed containment. In addition, the products and the intermediates may react with each other at high temperatures. As expected, the final products depend on the process conditions and contaminants. It is a challenging task to propose a complete mechanism and simulate the runaway process. It is also impractical because a thermal explosion will occur before the maximum temperature can be reached in most process conditions. Therefore, in this paper, Eqs. (1) and (2) were considered as the basis for the mechanisms we proposed.

4.2. Decomposition mechanism in alkaline medium

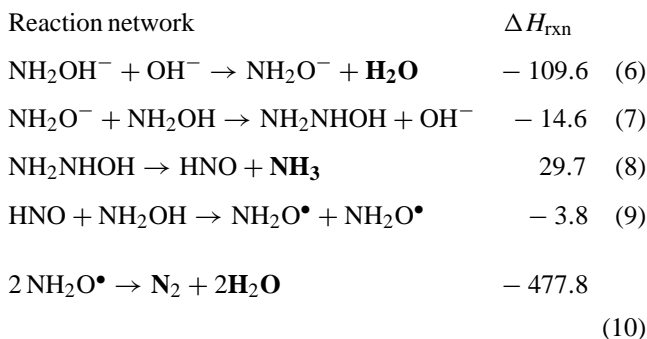
Hughes and Nicklin [18] studied the autoxidation of hydroxylamine in alkaline solutions and concluded that NH₂O⁻ was involved in the rate-limiting step. The reaction

scheme is given in Eqs. (4) and (5).



However, the recent study by Cisneros et al. [17] showed that air had no significant effect on the thermal decomposition of hydroxylamine solutions. The oxygen atoms in the products came from the hydroxylamine molecule.

The following simplified mechanism Eqs. (6)–(10) is proposed for hydroxylamine decomposition in alkaline solutions. The species in bold are the final products. Quantum chemical calculations were performed at the B3P86/cc-pVDZ level of theory using Gaussian 98. The enthalpies of reaction (ΔH_{rxn}) were calculated according to $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$, where H_{products} (kJ/mol) is the total enthalpies of products and $H_{\text{reactants}}$ is the total enthalpies of reactants.

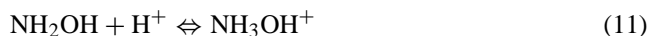


The reaction involves intermediates of NH_2O^- , NH_2NHOH , HNO , and radical NH_2O . The radical NH_2O is produced from the branching reaction, as shown in Eq. (9). The branching reaction is responsible for the explosive behavior of hydroxylamine decomposition because more intermediates are produced and the reaction rate is increased significantly. Adding both sides of Eqs. (6) to (10) and canceling the intermediates, the overall reaction is Eq. (1). Eq. (6) is exothermic and related to the initiation of the decomposition. With the increasing concentration of hydroxide ions, the reaction rate of Eq. (6) will increase and more heat will be released. This explains why the measured onset temperature decreases with the increasing pH. Applying steady-state assumption on all the intermediates, the concentration of HNO is proportional to that of hydroxide ions. So, the ratio of the branching reaction will also increase with pH, more NH_2O radicals will be produced, the reaction rate of Eq. (10) will be increased even more significantly because it is a second-order reaction, and therefore, more heat will be generated, and more nitrogen will be produced with the increasing concentration of hydroxide ions.

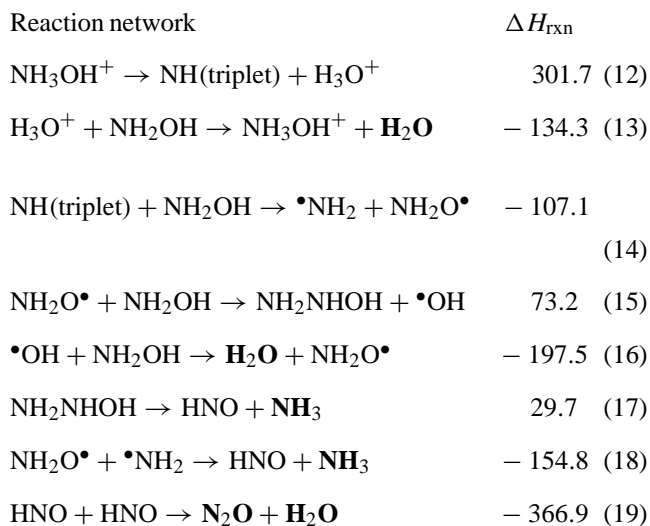
4.3. Decomposition mechanism in acid solutions

According to the study by Ebler and Schott [19], hydroxylamine exists as NH_2OH in alkaline and weakly acid solu-

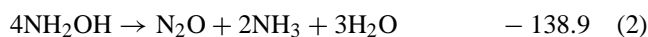
tions and normally acts as a reducing agent. In strongly acid solutions, it exists as H_3NO and acts as an oxidizing agent. In acid solutions, hydroxylamine is more likely to combine with the proton (H^+) than water (from Eq. (13)). The proton affinity of hydroxylamine was determined to be higher for protonation on nitrogen than on oxygen by experimental evaluation and theoretical calculation [14].



Eq. (11) is most likely when strong acid is mixed with hydroxylamine, although the heat of solvation was not detected by the APTAC because of the small amount of H^+ . Hydroxylamine and protonated hydroxylamine are in equilibrium under acidic conditions. When the concentration of the acid is much less than that of hydroxylamine, most of the hydroxylamine molecules exist as NH_2OH because it is more stable than H_3NO . From our experimental results, we conclude that the onset temperature decreases and maximum self-heat and pressure rates increase with the addition of acid. NH_3OH^+ must be responsible for the initiation reaction and can easily initiate decomposition as compared to NH_2OH , but further experimental analysis and quantum mechanical calculations are needed to verify it. The mechanism including Eqs. (12) to (19) is proposed based on information from the literature, Eq. (2), and chemical intuition.



The overall equation is



The decomposition pathway is more complicated than the one in alkaline medium. Besides the same intermediates of NH_2NHOH , HNO , $\text{NH}_2\text{O}^\bullet$ as in alkaline solutions, $\text{NH}(\text{triplet})$, H_3O^+ , $\bullet\text{NH}_2$, and $\bullet\text{OH}$ are also involved in the reactions. Eq. (12) was studied in detail by øiestad and Uggerud [20]. $\text{NH}(\text{triplet})$ was detected as the dominant product in the unimolecular decomposition of protonated hydroxylamine. $\text{NH}(\text{triplet})$ is more reactive than HNO with hydroxylamine and it plays an important role in the branching reaction. The difference of the branching reactions in

the two cases may explain why the maximum self-heat rate and pressure rate were higher in acid solutions than in alkaline solutions. Once the decomposition is initiated in acid solutions, $\text{NH}(\text{triplet})$ is produced and the branching reaction begins with heat-release, while in alkaline solutions, the branching reaction is less exothermic. The major gas product, N_2O is produced by the dimerization of HNO as shown in Eq. (19), which was studied thoroughly by Lin et al. [21] and Ruud et al. [22]. The calculated heat of reaction of -366.9 kJ/mol for Eq. (19) is in good agreement with the experimental value of -360.2 kJ/mol [23].

The heats of reaction were calculated at the B3P86/cc-pVDZ level of theory using Gaussian 98. All species were treated in the gas phase. The calculated overall heat of reaction of -138.9 kJ/mol is close to our experimental results (about -125.5 kJ/mol) even though the runaway reaction starts in the condensed phase.

5. Conclusions

The thermal decomposition of hydroxylamine with acid/base impurity was studied based on experimental results from the RSST and APTAC calorimeters and quantum mechanical calculations. Our studies have shown that thermal decomposition behavior of hydroxylamine is affected by the presence of acid or base. Two different decomposition reaction pathways can be initiated when acid or base is mixed with hydroxylamine. Hydrogen ion can increase the maximum self-heat and pressure rates while hydroxide ion can decrease the onset temperature and generate more gas products. Hydroxylamine must be handled and stored with caution because accidental mixing with impurities can pose an energy release hazard at lower temperatures. The mechanisms proposed in this paper provide a better understanding of hydroxylamine chemistry.

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