Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 414 (2004) 177–183
thermochimica acta
www.elsevier.com/locate/tca

Comparison of the thermal decomposition behavior for members of the hydroxylamine family

Lizbeth O. Cisneros, William J. Rogers, M. Sam Mannan*

Mary Kay O'Connor Process Safety Center, Chemical Engineering Department, Texas A&M University, College Station, TX 77843-3122, USA

Received 17 April 2003; received in revised form 10 September 2003; accepted 20 September 2003

Abstract

In the present work the thermal stability of some members of the hydroxylamine family was studied using adiabatic calorimetry. The study included aqueous solutions of hydroxylamine free base, hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-*o*-sulfonic acid of concentrations typically used in industry. Also, the catalytic effect of metal surfaces of stainless steel, carbon steel, and titanium was studied. From the solutions studied HA is the most reactive with higher maximum temperature, pressure, non-condensable pressure, and lower time to maximum rate. HA maximum heat rate is at least ∼3 times higher than that of the other solutions studied, and the pressure generation rate is ∼13 times higher. All decompositions were catalyzed by stainless steel, but only HA was catalyzed significantly by titanium metal. Solid hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-*o*-sulfonic acid exhibited stability up to ∼60 °C. Hydroxylamine 100% was not studied because it is not readily available, is not used industrially, and is known to be unstable at room temperature. A violent reaction was measured for solid hydroxylamine sulfate that generated a heat rate >500 °C/min and pressure rate >5200 psia/min before the sample cell was completely destroyed by the generated pressure.

Keywords: Hydroxylamine; Hydroxylamine hydrochloride; Hydroxylamine sulfate; Hydroxylamine-*o*-sulfonic acid; Adiabatic calorimetry; Thermal decomposition

1. Introduction

Hydroxylamine has been involved in two recent fatal incidents resulting in nine fatalities: Concept Sciences, Inc., in Pennsylvania and Nissin Chemical in Japan. After those incidents occurred, the need for thermal hazard information regarding hydroxylamine and hydroxylamine related components became evident. The Mary Kay O'Connor Process Safety Center is studying thermal hazards associated with members of the hydroxylamine components alone, in water solutions of commonly encountered industry concentrations, and in the presence of some metal contaminants.

2. Background

The components studied were hydroxylamine free base solutions, hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-*o*-sulfonic acid. Hydroxylammonium sulfate (hydroxylamine sulfate or oxammonium sulfate $(H_2NOH)_2H_2SO_4$) is the most common form of hydroxylamine used in industry. The commercially available solutions are 25 mass%, which is close to the maximum solubility limit at room temperature, and are transported in stainless steel containers. Hydroxylamine sulfate is also industrially available as a solid. Hydroxylamine hydrochloride is also commonly used industrially because hydroxylammonium salts either chloride or sulfates are more stable than the hydroxylamine free base (solid hydroxylamine free base is unstable at room temperature). Hydroxylamine-*o*-sulfonic acid is used as an intermediate for amination processes.

There exists some information regarding the thermal stability of hydroxylamine free base solutions [1–4]. Information about hydroxylamine sulfate thermal stability is scarce with the exception of a DTA study, which reports for the solid an onset temperature above 138 °C accompanied by gas evolution [5]. Thermal information regarding hydroxylamine hydrochloride and hydroxylamine-*o*-sulfonic acid is practically non-existent in the open literature [6]. This paper presents thermal hazard information obtained

---

* Corresponding author. Tel.: +1-979-862-3985; fax: +1-979-458-1493.
E-mail address: mannan@tamu.edu (M. Sam Mannan).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.09.023

under adiabatic runaway reaction conditions. The information includes onset temperatures, maximum temperatures, maximum pressures, non-condensable pressure, time to maximum rate, heat rates vs. temperature, and pressure rates vs. temperature. Also, the thermal behavior of aqueous solutions in the presence of titanium (Ti) and stainless steel (SS) metal surfaces are compared, and the effect of carbon steel as a nail contaminant added to the solutions is presented.

3. Experimental details

3.1. Samples

3.1.1. Solids

The solids studied were Aldrich hydroxylamine hydrochloride 99.9999 mass% catalog number 37992-1 [$H_2NOH\cdot HCl$], Aldrich hydroxylamine sulfate 99.9999% catalog number 37991-3 [$(H_2NOH)_2(H_2SO_4)$], and Aldrich 99.999% hydroxylamine-*o*-sulfonic acid catalog number 48097-5 [H_2NOSO_3H].

3.1.2. Aqueous solutions

The solutions studied were Aldrich hydroxylamine 99.999% 50 mass% solution in water (HA) catalog number 46780-4, hydroxylamine hydrochloride/water 35 mass% (HH), hydroxylamine sulfate/water 25 mass% (HS), and hydroxylamine-*o*-sulfonic acid 35 mass% solution in water (HOSA). All the solutions were prepared from the corresponding solid and Aldrich reagent water catalog number 32007-2. These particular solution concentrations are the highest industrially available.

3.2. Apparatus

Measurements reported here were performed in an automatic pressure tracking adiabatic calorimeter (ATPAC) [7]. This apparatus permits the measurements of runaway reaction behavior under adiabatic conditions and during an experiment, the pressure inside the sample cell is compensated with N_2 in the space surrounding the sample cell, which can be made from materials that do not withstand large pressure differentials such as glass. The data recorded during an experiment are time, temperature, pressure, heat rate, and pressure rate. The APTAC can follow a reaction adiabatically up to 400 °C/min and can compensate pressure increases up to 10,000 psi/min.

3.3. Analytical methods

The gaseous products were also analyzed using a gas chromatograph (GC), since the possible H_2 contained in the decomposition products cannot be detected in the EI-FTMS. The chromatograph was a Varian 3400 with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The sample size was 0.5 ml for the TCD side and 0.25 ml for the FID side. A Chromsorb 107 (12 feet × 1/8 in., 80/100) and a 13× molecular sieve (6 feet × 1/8 feet, 40/60) columns were used on the TCD side. An alumina plot capillary column ($40\,m \times 0.53\,mm \times 15\,\mu m$) was used on the FID side. Four switching valves were used to facilitate sampling and column selection. The temperature program used was as follows: 4 min at 35 °C, then a 10 °C/min ramp until 200 °C, and finally 20 min at 200 °C. Only the TCD detector was useful for the particular gas mixture, since no peaks were detected by the FID.

Liquid products were analyzed for ammonia and water. The ammonia quantification method consisted of adding MgO to the ammonia-containing sample and titrating the resulting mixture with NaOH with methyl red as an indicator [8]. The water content of the liquid residue was analyzed using a Karl Fischer moisture method [9].

3.4. Experimental method

The experiments reported here were performed in a closed cell environment with air above the sample. The heating mode was heat–wait–search, in which the sample was heated to an initial search temperature (50 °C) and the temperature was allowed to stabilize (20 min). Then if exothermic activity was detected, as exhibited by a threshold sample temperature rise of ~0.1 °C/min, the apparatus followed the reaction adiabatically until the reaction ended or until one of the pre-selected safety shutdown criteria was met (shutdown criteria: temperature 460 °C; pressure 10,342 kPa (1500 psia); temperature rate 400 °C/min; pressure rate ~68,900 kPa/min (10,000 psia/min)). If no exothermic activity was detected within 20 min, the sample was heated to the next search temperature and the procedure was repeated until a preset maximum search temperature was reached (250 °C).

Samples were transferred to sample cells using disposable plastic pipettes. Sample masses were obtained by weight differences. A sample thermocouple with a Teflon-coated sheath and a total diameter of ~1/16 in. was used to prevent the thermocouple metal surface from contacting the sample, which may be catalyzed by metals as in the case of hydroxylamine free base [2].

Experimental runs were performed in spherical sample cells of 130 cm^3 nominal volume and of borosilicate glass, stainless steel 316 (SS), and titanium (Ti). It was presumed that glass cells provided a neutral environment without significant catalysis for the decomposition reactions. Reactivity with respect to the other materials (SS and Ti) was tested by using the corresponding cells.

Experiments were performed to test the effect of carbon steel (composed primarily of iron, 97–99%, and graphite, <2%), which is a common industrial contaminant that is found in nails, wire, or structural components. A piece of carbon steel nail (~0.15 g) was introduced into some samples after the sample was weighed in a glass cell.

3.5. *Uncertainties*

A type N thermocouple was used to measure sample temperatures with an overall absolute uncertainty of ∼±1 °C, and checked periodically at 0 °C using an ice bath. Sample pressures were measured with Sensotec absolute pressure transducers with an overall uncertainty of ∼±42 kPa (∼6 psia) and checked frequently for agreement with ambient pressures. Sample masses were measured with a precision of ±0.01 g.

4. Results and discussion

4.1. *HA, HH, HS, and HOSA thermal decomposition behavior in glass*

Table 1 presents a compilation of measured parameters based on an initial solute mass of approximately 1.1 g. With the exception of HOSA first exothermic activity, HA has the lowest onset temperature. Analysis of Table 1 shows that, in the event of a runaway, HA will pose the greatest risk, since it is able to generate higher temperature, pressure, and non-condensable pressure.

A summary of the heat and pressure rates is presented in Table 2. Information in Table 1 qualitatively suggests that hydroxylamine free base will release a greater amount of energy per unit mass, since the adiabatic temperature increase was higher even when a significant amount of the released heat was consumed to vaporize the solvent and reach a greater equilibrium vapor pressure. A discussion concerning the heat of hydroxylamine decomposition determined from the measured heat of reaction and temperature rise is available in an earlier article [3]. With the additional information presented in Table 2, it is evident that not only the heat released per unit mass of hydroxylamine is greater but also that it is liberated faster. The rate of energy release is a critical issue when evaluating thermal hazard; after all, a runaway reaction is created when the heat produced by the reaction cannot be removed fast enough by the cooling system. Based on analysis of the gas phase decomposition products, an overall decomposition reaction for hydroxylamine was presented in an earlier article [4].

The heat rate vs. temperature behavior is presented in Fig. 1, which shows that the studied members of the hydroxylamine family exhibit exothermic activity between ∼100 and 220 °C. For this range of temperature, HA presents the most aggressive reaction with a heat rate 7.6 times greater than that of HH, which presents the second most aggressive reaction. HOSA has its first and most violent exothermic activity beginning at ∼50 °C with a maximum heat rate of ∼1.4 °C/min.

Table 2
Thermal decomposition rates for some hydroxylamine family members

Sample[a]	dT/dt_{max} (°C/min)	dP/dt_{max} (psi/min)
HA, 50 mass%	4.5 ± 1.0	20 ± 3
HH, 35 mass%	0.59 ± 0.38	1.51 ± 0.76
HS, 25 mass%	0.11 ± 0.02	0.32 ± 0.06
HOSA, 35 mass%	1.41 ± 0.67	0.33 ± 0.32

[a] Aqueous solutions.

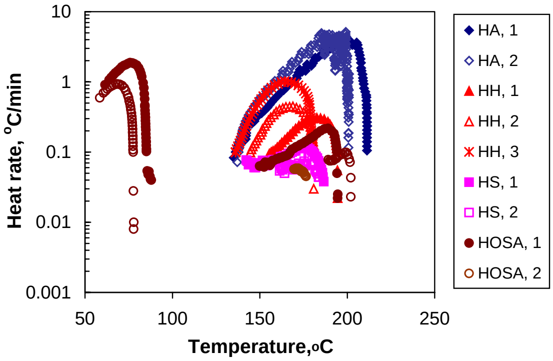

Fig. 1. Measured heat rates for some hydroxylamine family members.

Fig. 2 presents the pressure rate for the solutions studied. As shown in this graphic, HA has the greatest pressure rate followed by HH, HOSA, and HS in that order. It is important to note that although HOSA was second in the heat generation rate, it is not second with respect to the pressure generation rate. This observation can be explained by the fact that the most aggressive exothermic behavior for HOSA occurs at low temperatures, where the solvent vapor pressure is low and the produced heat is utilized to heat the sample instead of vaporizing the solvent. The pressure generation rate for HA is more than 13 times greater than that of HH.

4.2. *Solid hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-o-sulfonic acid thermal behavior*

The thermal analysis of pure hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-*o*-sulfonic

Table 1
Decomposition parameters for some hydroxylamine family members

Sample[a]	T_{on} (°C)	T_{max} (°C)	ΔT_{adb} (°C)	P_{max} (psia)	Non-cond. (psia)	t_{MR} (min)
HA, 50 mass%	136 ± 1	207 ± 6	71 ± 7	338 ± 41	44 ± 5	87 ± 35
HH, 35 mass%	145 ± 10	185 ± 8	40 ± 4	99 ± 17	25 ± 9	101 ± 40
HS, 25 mass%	152 ± 14	185 ± 2	34 ± 15	188 ± 10	10.6 ± 0.4	325 ± 93
HOSA, 35 mass%	<50[b], 160 ± 14	90[b], 198 ± 5	40[b], 40 ± 9	191 ± 22	13 ± 3	328 ± 51

[a] Aqueous solutions.
[b] Refers to the first HOSA exothermic activity.

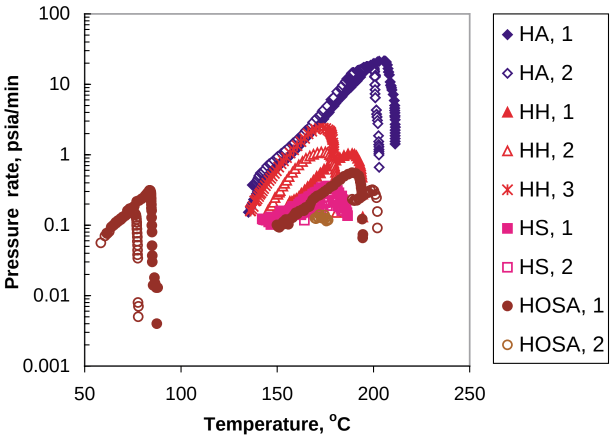

Fig. 2. Measured pressure rates for some hydroxylamine family members.

acid produced surprising results, since the least reactive solution, HS, turned out to be the most reactive solid. HS solutions presented maximum heat and pressure rates of only 0.62 °C/min and 5.39 psi/min, respectively, even when 40 g of HS (10 g of hydroxylamine sulfate) was tested. As shown in the temperature and pressure profiles of Figs. 3 and 4, respectively, hydroxylamine sulfate has a dramatically more reactive behavior when compared to hydroxylamine hydrochloride and hydroxylamine-*o*-sulfonic acid. It is important to note that solid 100% hydroxylamine was not tested, and, most probably, it would have resulted in an even more violent reaction than the hydroxylamine sulfate, because 100% hydroxylamine is known to decompose violently at room temperature.

Table 3 presents a summary of the decomposition parameters for the studied solids. It can be seen from this table that the hydroxylamine sulfate not only has the highest reaction onset temperature but also the most violent decomposition. This observation stresses the importance of experimental work to test for reactivity, since there is no correlation between reaction onset temperature and rate of energy release.

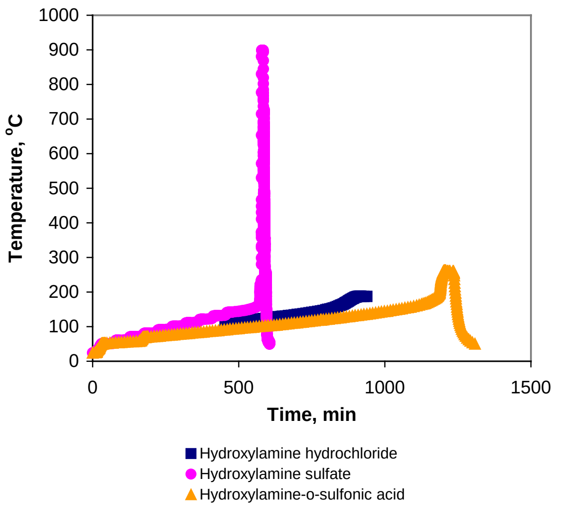

Fig. 3. Temperature profile for some hydroxylamine family members. Solid 100% concentration.

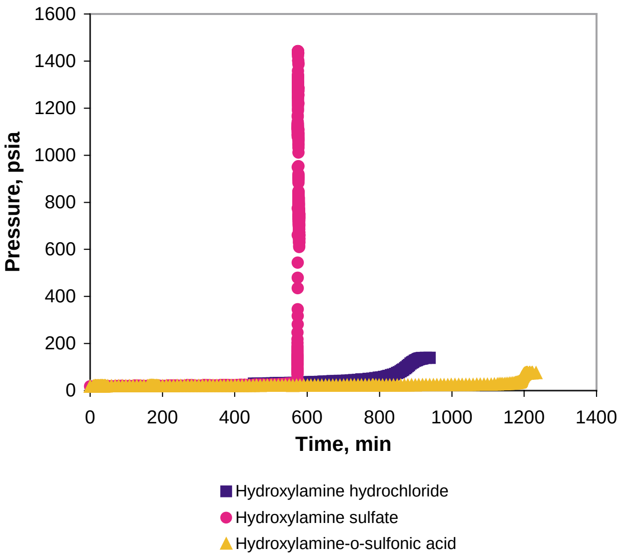

Fig. 4. Pressure profile for some hydroxylamine family members. Solid 100% concentration.

Figs. 5 and 6 present the heat and pressure rates for the studied solids, respectively. It can be seen that solid hydroxylamine-*o*-sulfonic acid has a far more aggressive heat and pressure generation rates than that of hydroxylamine hydrochloride solid. This is another example of the importance of experimental work, because behavior in solution cannot be predicted from behavior of the solid.

4.3. HA, HH, HS, and HOSA behavior in the presence of metals

4.3.1. Nail test

Fig. 7 presents the heat rates produced when a similar piece of carbon steel in the form of a nail was added to

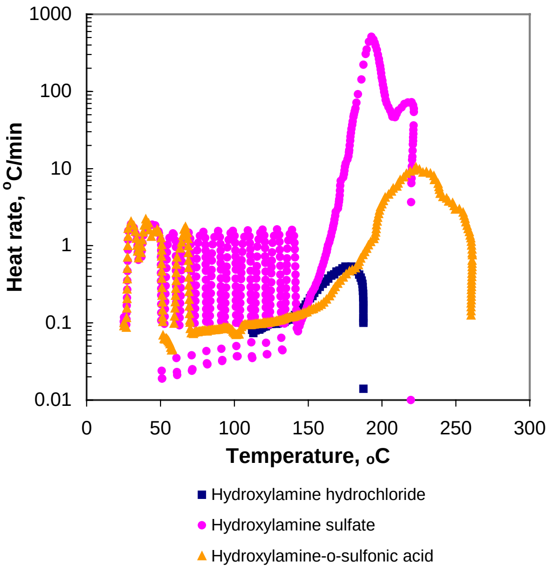

Fig. 5. Heat rate for some hydroxylamine family members. Solid 100% concentration.

Table 3
Measured parameters for some hydroxylamine family members

Sample[a]	Mass (g)	T_{on} (°C)	T_{max} (°C)	P_{max} (psia)	Non-cond. (psia)	dT/dt_{max} (°C/min)	dP/dt_{max} (psi/min)
Hydroxylamine hydrochloride	1.22	112	187	139	80.9	0.54	1.28
Hydroxylamine sulfate	1.58	144	NM[b]	NM[b]	NM[b]	>500	>5200
Hydroxylamine-*o*-sulfonic acid	1.58	71.5	259	74	19	10.4	3.07

[a] Pure solids.
[b] Not measured due to cell rupture.

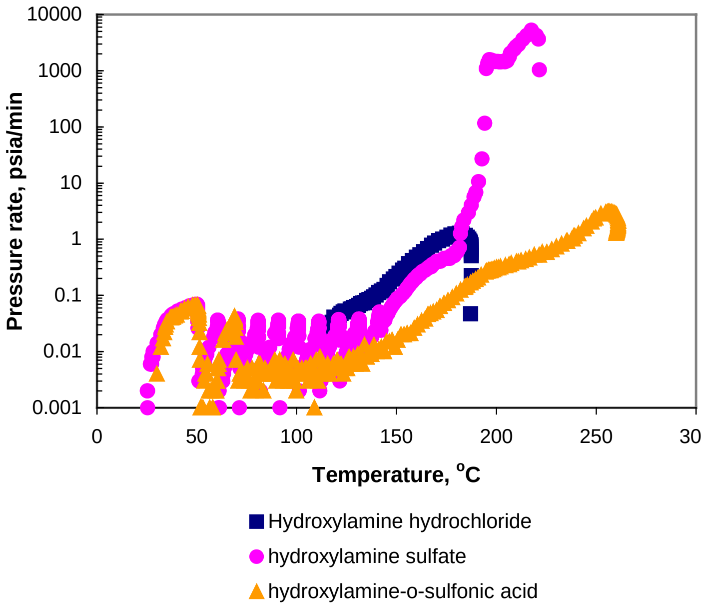

Fig. 6. Pressure rate for some hydroxylamine family members. Solid 100% concentration.

HA, HH, and HOSA. Carbon steel catalyzed the three solutions, and the apparent low heat generation of HOSA can be misleading since HOSA started to react as soon as the nail contacted the solution, so most of the exothermic behavior was not measured. In fact, based on what was observed in the laboratory it is safe to assume that HOSA reacted more aggressively when contacting the nail than HH and HA. HA and HH had similar reaction rates but the HA reaction proceeded for a longer period of time. In the case of HH and HOSA, the measured heat rates included not only the decomposition reaction but also the reaction between the acid media and the carbon steel, since in both cases the nail was completely dissolved at the end of the experiment.

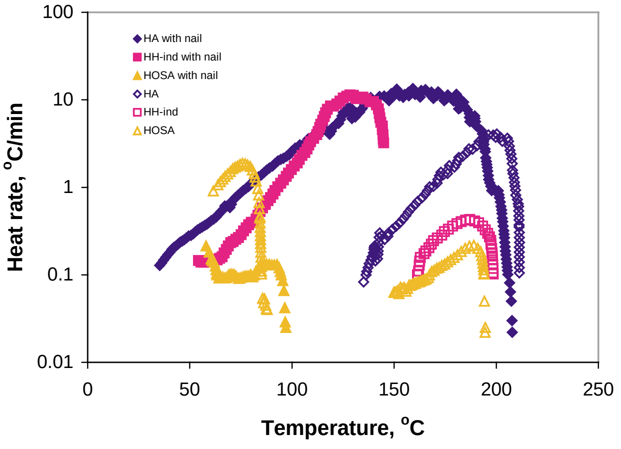

Fig. 7. Heat rate for hydroxylamine solutions with and without carbon steel in the form of a nail.

4.3.2. *Test in stainless steel (SS) and titanium (Ti) sample cells*

Table 4 presents a summary of the maximum heat rates attained by HA, HH, and HOSA in glass, SS, and Ti test cells. HS data are not included in the table since no appreciable exothermic behavior was detected for HS decomposition in SS or titanium. Table 4 presents also the ratio of maximum

Table 4
Maximum heat rate for HA, HH, and HOSA in several test cell materials

Sample[a]	dT/dt_{max} (°C/min)			$(\mathrm{d}T/\mathrm{d}t)_{max}/(\mathrm{d}T/\mathrm{d}t)_{max\ glass}$	
	Glass	SS	Ti	SS	Ti
HA, 50 mass%	4	77	100	19.3	25
HH, 35 mass%	0.6	4.1	0.6	6.9	1
HOSA, 35 mass%	1.4	27	3.1	19.1	2

[a] Aqueous solutions.

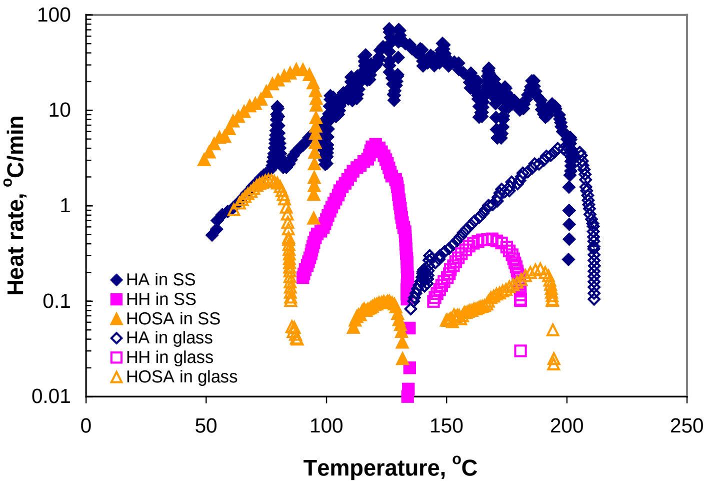

Fig. 8. Effect of SS in the decomposition reaction of various hydroxylamine solutions.

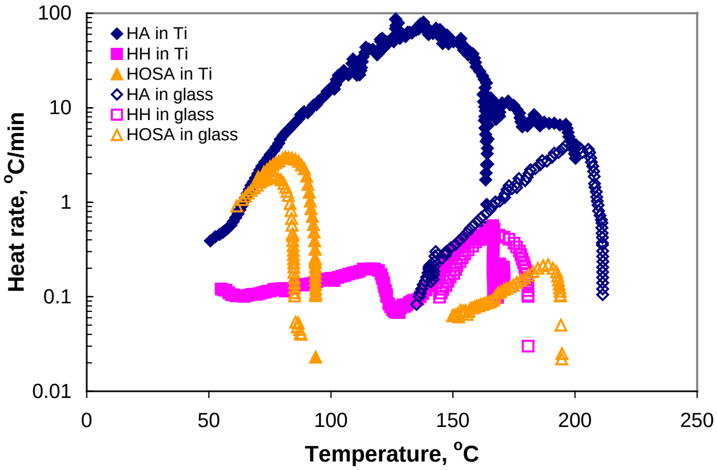

Fig. 9. Effect of Ti in the decomposition reaction of various hydroxylamine solutions.

heat rate in a metal cell to maximum heat rate in glass. As can be seen in the table, SS catalyzes HA decomposition as much as Ti does. For the HH decomposition, there is a significant difference between SS and Ti, since Ti has almost a null catalytic effect, whereas SS increases the maximum rate almost seven times. For HOSA, SS increases the maximum heating rate 19 times and Ti increases the maximum heating rate 2 times.

Fig. 8 presents the heat rate vs. temperature for the samples in SS cell. It can be seen that the effect of SS metal upon contact with HA, HH, or HOSA is to increase the heat rates. Fig. 9 presents the effect of Ti in the decomposition reaction of various hydroxylamine solutions. It can be seen from this graphic that, except for HA, the effect of Ti in the thermal decomposition in not so drastic as for SS. Ti is known for its inert qualities so it was surprising to observe that Ti catalyzes the HA decomposition reaction.

4.4. Kinetic comparison

Table 5 presents the activation energy and reaction order obtained when a power law kinetic model was applied to the exothermic behavior of the various hydroxylamine solutions studied [2]. The least reactive substance, HS, has the highest overall activation energy, but the more reactive solution, HA, has a higher activation energy than HH. The HA activation energy (28.5 kcal/mol) is lower than the energy required to break the H_2N–OH (61.3 kcal/mol) bond, so correlations based on the weakest bond breakage as a way to predict reactivity cannot be applied to the HA system. The higher dependence of HS decomposition rate on concentration represented by a reaction order of two may be due to the presence of two hydroxy-

Table 5
Comparison of kinetic parameters for four members of the hydroxylamine family

Sample[a]	E_a (kcal/mol)	p
HA, 50 mass%	28.5	1
HH, 35 mass%	25	0.5
HS, 25 mass%	43	2
HOSA, 35 mass%	31	0.7

[a] Aqueous solutions.

Table 6
Gas phase analysis for HA and HH

Sample[a]	N_2 (mol%)	NO (mol%)	O_2 (mol%)	N_2O (mol%)	H_2 (mol%)
HA, 50 mass%	70	4	–	24	2
HH, 35 mass%	64.8	0.9	16.8	8.5	9

[a] Aqueous solutions.

Table 7
Comparison of liquid phase analysis for four hydroxylamine solutions

Sample[a]	Ammonia (mass%)	Water (mass%)	Unaccounted (mass%)
HA, 50 mass%	7.9	92.3	2.8
HH, 35 mass%	4.1	72.4	23.5
HS, 25 mass%	1.8	82	16.2
HOSA, 35 mass%	1.9	59	39.1

[a] Aqueous solutions.

lamine free base molecules in each hydroxylamine sulfate molecule.

4.5. Comparison of the analytical results

Gas phase analyses were performed only in HA and HH samples, and the results are presented in Table 6. As expected, the HH sample produced more hydrogen. The concentration of nitrogen in the gas phase remained almost the same for HA and HH, but the N_2O concentration was lower in the HH sample. The HH sample produced oxygen that was not measured in the HA decomposition gaseous products.

Table 7 presents the results for the analysis of the liquid phase residues for the various hydroxylamine derivatives. As shown in the table, all of them produced ammonia. HA and HH had a higher ammonia mass% than that of HS and HOSA. For HA the unaccounted for mass% was only 2.8 mass% but for HH and HOSA it was over 20 mass%.

5. Conclusions

From the solutions studied HA is the most reactive having higher maximum temperature, pressure, non-condensable pressure, and lower time to maximum rate. HA maximum heat rate is at least ~3 times higher than the other solutions studied and the pressure generation rate is ~13 times higher. All decompositions were catalyzed by stainless steel but only HA was dramatically catalyzed by titanium metal.

Solid hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-*o*-sulfonic acid were studied and all of them were stable up to ~60 °C. Hydroxylamine 100% was not studied because it is not readily available and is not used industrially, but it is known to be unstable at room temperature. Solid hydroxylamine sulfate had a violent reaction that generated a heat rate >500 °C/min and pressure rate >5200 psia/min before the sample cell was completely destroyed.

Acknowledgements

We thank CONACYT for its financial support. This research was sponsored by the Mary Kay O'Connor Process Safety Center at Texas A&M University.

References

[1] H. Surjono, Z. Xiao, P.C. Sundareswaran, Z. Zhe, Understanding thermal stability of hydroxylamine free base, in: Proceedings of the 218th ACS National Meeting, New Orleans, USA, 1999.

[2] L.O. Cisneros, W.J. Rogers, M.S. Mannan, J. Hazard. Mater. 82 (2001) 13.

[3] L.O. Cisneros, W.J. Rogers, M.S. Mannan, Effect of air in the thermal decomposition of 50 mass% hydroxylamine/water, J. Hazard. Mater. 95 (1–2) (2002) 13–25.

[4] L.O. Cisneros, X. Wu, W.J. Rogers, M.S. Mannan, J. Park, S. North, Decomposition products of 50 mass% hydroxylamine/water under runaway reaction conditions, in: Transactions of the Institute of Chemical Engineers on Process Safety and Environmental Protection, vol. 81, Part B, March 2003, pp. 121–124.

[5] J. Ritz, H. Fuchs, Hydroxylamine, in: Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., vol. A13, Weinheim, Federal Republic of Germany, 1985, pp. 527–532.

[6] L.O. Cisneros, Adiabatic calorimetric studies of hydroxylamine compounds, Ph.D. Chemical Engineering Dissertation, Texas A&M University, August 2002.

[7] S. Chippett, P. Ralbovsky, R. Granville, The APTAC: a high pressure, low thermal inertia, adiabatic calorimeter, in: Proceedings of the International Symposium on Runaway React, Pressure Relief Des., Effluent Handling, 1998, pp. 81–108.

[8] W. Horowitz, Official Methods of Analysis of AOAC International, 17th ed., Method Number 920.03.

[9] W. Horowitz, Official Methods of Analysis of AOAC International, 17th ed., Method Number 966.20.