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Adiabatic calorimetric decomposition studies of 50 wt.% hydroxylamine/water

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Abstract

Calorimetric data can provide a basis for determining potential hazards in reactions, storage, and transportation of process chemicals. This work provides calorimetric data for the thermal decomposition behavior in air of 50 wt.% hydroxylamine/water (HA), both with and without added stabilizers, which was measured in closed cells with an automatic pressure tracking adiabatic calorimeter (APTAC). Among the data provided are onset temperatures, reaction order, activation energies, pressures of noncondensable products, thermal stability at 100°C, and the effect of HA storage time. Discussed also are the catalytic effects of carbon steel, stainless steel, stainless steel with silica coating, inconel, titanium, and titanium with silica coating on the reaction self-heat rates and onset temperatures. In borosilicate glass cells, HA was relatively stable at temperatures up to 133°C, where the HA decomposition self-heat rate reached 0.05°C/min. The added stabilizers appeared to reduce HA decomposition rates in glass cells and at ambient temperatures. The tested metals and metal surfaces coated with silica acted as catalysts to lower the onset temperatures and increase the self-heat rates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxylamine; Thermal decomposition; Adiabatic calorimetry; APTAC; Metal contamination

1. Introduction

Because chemical reactions often generate thermal energy, understanding the behavior of process reaction systems is essential for plant safety. Adiabatic calorimetry can provide information for design of safe processes, storage, and transportation of chemicals. This work presents calorimetric data for the decomposition of 50 wt.% hydroxylamine/water (HA) in glass and in the presence of several metals. Although HA is widely used in the electronics

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and pharmaceutical industries, very little information about its thermal decomposition is available [1].

Hydroxylamine was involved in two recent accidents: an explosion at Concept Sciences Inc. chemical plant near Allentown, Pennsylvania on 19 February 1999, killed five people, injured at least 13, and destroyed a 45,000 ft^2 structure. On 16 June 2000, an explosion at Nissin Chemical in Japan killed four, injured 25, and destroyed the plant. Although the root causes of these incidents have not yet been established, these tragic accidents stress the importance of obtaining information about the reactive behavior of chemicals, such as HA, and the potential role of metal contaminants as catalysts for the design of safe industrial processes.

Calorimetry is used to study the thermal behavior and, therefore, to evaluate the potential hazards of chemical reactions. The two main types of calorimeters in current industrial use are screening and adiabatic. Screening calorimeters such as the reactive system screening tool (RSST) [2] are used for rapid tests of systems for thermal hazards. In general, only materials that have shown potential hazards with a screening method are evaluated using adiabatic calorimetry, because the time and costs of tests associated with adiabatic calorimetry are usually much higher [3]. A discussion of these two calorimeters together with a comparison of results produced by them is provided by Leung and Fisher [4].

Adiabatic calorimetry yields reaction rate information, which is needed for chemical process strategies such as determining time available to control a process, set alarms or, in a critical case, evacuate. The present work presents reaction rate information about the overall HA decomposition reaction in glass cells.

2. Background

A power law rate expression can describe the overall decomposition reaction of HA,

$$\frac{\mathrm{d[HA]}}{\mathrm{d}t} = -k[\mathrm{HA}]^n, \tag{1}$$

where [HA] is the concentration of HA, t the time, k the rate constant, and n is the reaction order.

In an adiabatic experiment with an exothermic reaction, sample temperature is increased until the onset temperature, T_o, is detected. For the present study, the onset temperature is defined as the temperature at which the heat of reaction produces a sample temperature rate of 0.05°C/min. Because the sample is maintained during the reaction in a nearly adiabatic state, the heat generated by the reaction increases the sample temperature and, therefore, increases the reaction rate constant. The Arrhenius equation provides a simple expression for the dependence of the reaction rate constant on sample temperature

$$k = A\,\mathrm{e}^{-E_\mathrm{a}/RT}, \tag{2}$$

where A is the frequency factor, E_a the activation energy, R the gas constant, and T is the temperature.

During an exothermic reaction, higher temperatures increase the reaction rate constant as the sample concentration decreases. T_max is defined as the temperature at which the

reaction stops due to depletion of the reactants. Then, assuming an adiabatic reaction in a single phase, the concentration can be approximately related to any temperature between T_o and T_{max} by the following equation:

$$[HA] = \frac{T_{max} - T}{T_{max} - T_o}[HA]_0, \tag{3}$$

where $[HA]_0$ is the initial concentration of HA, T_{max} the maximum adiabatic temperature, and T_o is the onset temperature.

Using Eqs. (1) and (3), an expression for the pseudo-kinetic constant, $k'(k' = [HA]_0^{n-1}k)$ is obtained [5] as:

$$k' = \frac{dT/dt}{((T_{max} - T)/(T_{max} - T_o))^n (T_{max} - T_o)}, \tag{4}$$

where (dT/dt), T_{max}, and T_o are measured experimentally. With an initial value for the reaction order, k' can be calculated from Eq. (4). An Arrhenius plot ($\ln k'$ versus $1/T$) yields a straight line if the correct reaction order is employed.

An important parameter in adiabatic calorimetry is the ϕ factor, which is defined as:

$$\phi = 1 + \frac{M_c C_c}{M_s C_s},$$

where M_c is the sample cell mass, M_s the sample mass, C_c the sample cell specific heat, and C_s is the sample specific heat. More detailed analyses of adiabatic calorimetric data are available elsewhere [5,6].

Participation of metal surfaces of the spherical cells as catalysts in the HA decomposition reaction was suspected, so the ratio of metal surface contact area to sample volume (SVR) was calculated as a measure of catalyst area.

$$SVR = \frac{2\pi rh}{V},$$

where V is the sample volume, r the cell internal radius, and h is the sample height, which was calculated from the following equation:

$$\tfrac{1}{3}\pi h^3 - (r\pi)h^2 + V = 0$$

The SVR values for a cabon steel nail and for a thermocouple sheath, as presented below, were calculated using the corresponding metal surface areas and sample volumes in the sample cells.

3. Experimental details

3.1. Samples

Two sources of 50 wt.% HA were used in the present study: Aldrich hydroxylamine 99.999% 50 wt.% solution in water, catalog No. 46,780-4, and hydroxylamine 50 wt.%

solution in water with added stabilizers, supplied by an industrial source. The Aldrich hydroxylamine samples featured a nominal high purity and contained no added stabilizers. All HA samples were used in the received condition without further analysis or purification.

3.2. Apparatus

Measurements reported here were made with an APTAC, which is described in detail elsewhere [7]. Open and closed cell experiments are possible and several modes of heating (e.g. adiabatic, isothermal, ramped) can be programmed. During an experiment, values for time, temperature, pressure, heat rate, pressure rate, and other variables are measured and recorded. Because the pressure outside the sample cell is controlled to match the pressure inside the cell, glass cells and sample cells with low thermal inertia can be used. The frequency of data measurement depends on sample activity and can vary from every 10 min to less than 1 s.

3.3. Experimental method

For the present work, all experiments were performed in a closed cell environment with ambient air above the sample. Two different types of heating modes were used: heat-wait-search and isothermal. In the heat-wait-search mode, the sample was heated to an initial search temperature and the temperature was allowed to stabilize (20 min). Then if exothermic activity was detected, as exhibited by a threshold sample temperature rise of 0.05°C/min, the apparatus followed the reaction adiabatically until the reaction ended or until one of the pre-selected safety shutdown criteria was met. 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. In the isothermal mode, the sample temperature was held at 100°C for 3 days to test for thermal stability as indicated by the rate of pressure increase.

HA samples were transferred to sample cells using disposable plastic pipettes. Because of the small sample amounts, no sample stirrer was used in the sample cells. A sample thermocouple with a Teflon-coated sheath was used to prevent the metal surface from contacting the sample. An inconel-sheath sample thermocouple without Teflon coating was used in two experiments discussed below.

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

Experiments were performed to test the effect of carbon steel (composed primarily of iron, 97–99%, graphite, $<2\%$), which is a common industrial contaminant that is found in nails, wire, or structural components. A piece of carbon steel nail with a ratio of nail surface area to sample volume (SVR) of $\sim 0.024\,mm^{-1}$ was introduced into the sample after the sample was weighed in a glass cell.

3.4. Uncertainties

A type N thermocouple was used to measure sample temperatures with an overall absolute uncertainty of ∼±1°C, and was frequently checked at 0°C using an ice bath. Sample pressures were measured with Sensotec absolute pressures transducers within an overall uncertainty of∼±2 psi and were frequently checked for agreement with ambient pressures. Sample weights were measured with an accuracy to within ±0.01 g.

4. Results and discussion

4.1. HA experiments in glass cells

Heat-wait-search experiments were performed to obtain onset temperatures, lumped kinetics of the overall decomposition reaction system, heat generation rates, pressure generation rates, and pressures of noncondensable products. Fig. 1 shows a typical plot of temperature as a function of time for a HA decomposition test with the search mode of the APTAC above and below the HA exotherm region. Because the sample cell absorbs some of the generated thermal energy, the use of relatively high nominal ϕ factors (3.6–6) was needed to follow the exothermic decompositions to completion. Although onset temperatures are not a significant function of ϕ factors, the final temperatures, heat rates, and pressure rates are dependent on ϕ, and these values are not directly scaleable [8].

A summary of the decomposition tests in borosilicate glass cells is presented in Table 1. Values are reported with a standard deviation calculated from three experimental replicas for HA samples with stabilizers, W, and the difference between two experimental replicas for samples without stabilizers, WO. As shown, there is no significant difference in the onset temperature of the HA thermal decomposition reaction with and without stabilizers. The heat generation rate is higher in samples without stabilizers than in samples with stabilizers, but this difference did not significantly affect the calculated activation energy within the

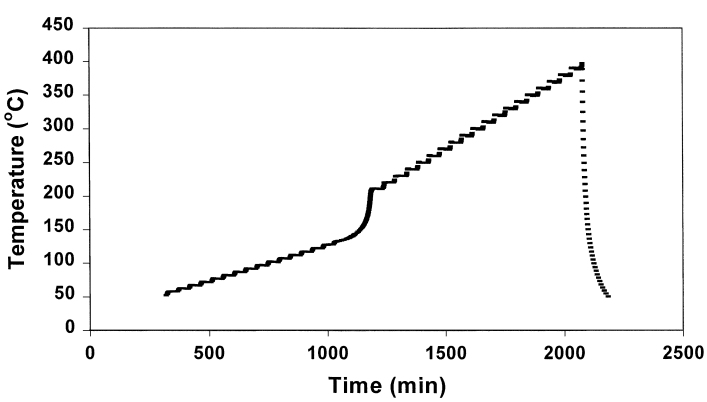

Fig. 1. Typical temperature vs. time plot for the decomposition of 50 wt.% hydroxylamine/water in a glass cell.

Table 1
HA decomposition tests in glass cells

Sample	Replicas	T_o (°C)	T_{max} (°C)	P_{max} (psia)	$(\Delta T/\Delta t)_{max}$ (°C/min)	$(\Delta P/\Delta t)_{max}$ (psia/min)	E_a (kcal/mol)
WO	2	136 ± 1	207 ± 5	338 ± 29	4.5 ± 1.0	20 ± 2	34 ± 4
W	3	133 ± 2	216 ± 8	402 ± 45	1.9 ± 0.7	27 ± 34	29 ± 4

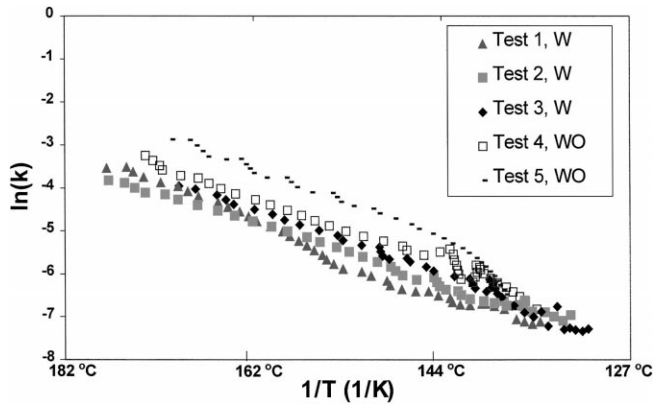

Fig. 2. HA with stabilizers (W) and without stabilizers (WO) decomposition kinetics (50% of reaction) in glass cells.

experimental uncertainty. Fig. 2 shows the decomposition kinetics plot of HA for the first half of the overall reaction, which can be represented approximately as first-order.

The noncondensable pressure generated was ∼47 psia at 50°C for both kinds of samples with a remaining liquid weight of 74–60% of the initial sample weight. The final color was bluish for the HA with stabilizers and green-bluish or teal for the HA without stabilizers.

The thermal stability of HA with stabilizers at 100°C was tested over a period of 3 days, as shown in Fig. 3. A summary of the tests is presented in Table 2, which shows that the HA with stabilizers reacted slowly at this temperature, as determined by the average pressure generation rate and by the total noncondensable pressure produced during the experiments (26–29 psia at 100°C). The appearance of the sample remaining was clear as in the beginning of the experiment.

4.1.1. Effect of HA storage time

HA without stabilizers decomposes over time even at sub-ambient temperatures. Stored at 10°C for a period of 5 months, an industrial sample without stabilizers generated gaseous

Table 2
Stability tests of W samples at 100°C in glass cells

Sample (g)	Time (h)	Initial pressure (psia)	Final pressure (psia)	Average $(\Delta P/\Delta t)$ (psia/h)
2.28	72.0	27	56	0.40
2.22	73.5	28	54	0.34

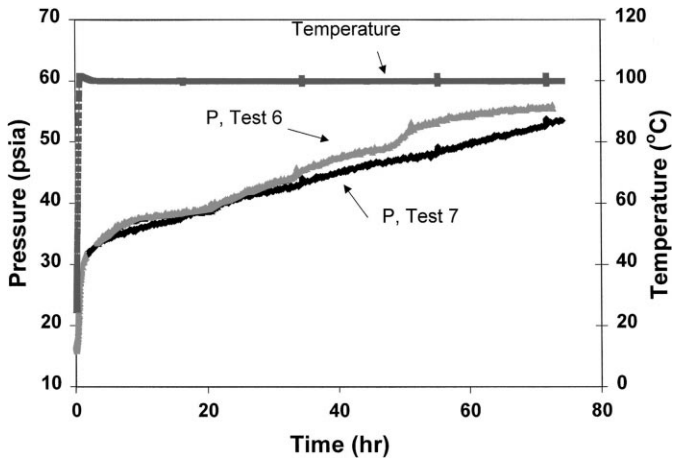

Fig. 3. HA with stabilizers (W) stability tests at 100°C in glass cells.

decomposition products that expanded the plastic container. An Aldrich HA sample, 99.999% 50 wt.% solution in water, that had been stored at 10°C for 5 months was tested in a glass cell. As shown in Fig. 4, this older sample exhibited a much more energetic decomposition with an onset temperature of 67°C and a maximum self-heat rate of 132°C/min compared with an onset temperature of 136°C and a maximum self-heat rate of 5°C/min for a recently received or "new" sample.

4.2. Effect of various metals and silica coating on HA decomposition

4.2.1. Inconel sheath thermocouple

As summarized in Table 3, two heat-wait-search experiments of HA with stabilizers using a thermocouple with an inconel sheath without Teflon coating compared with three tests

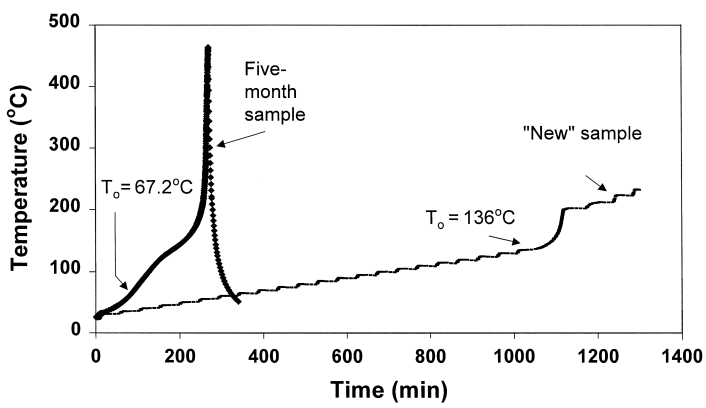

Fig. 4. HA without stabilizers decomposition tests in glass cells for a "new" sample and for a sample following storage at 10°C for 5 months.

Table 3
Effect of inconel sheath thermocouple on onset temperature for W samples in glass cells

Thermocouple	Replicas	Average T_o (°C)	$(\Delta T/\Delta t)$ at 120°C (°C/min)	$(\Delta T/\Delta t)$ at 135°C (°C/min)	$(\Delta T/\Delta t)$ at 150°C (°C/min)
Inconel sheath	2	122.0	0.05	0.11	0.38
Teflon coated sheath	3	133.0	0.03	0.08	0.22

using a Teflon coated thermocouple demonstrated the effect of the inconel sheath material as a catalyst in the HA decomposition reaction. The thermocouple sheath was ∼2 mm beneath the liquid surface yielding a SVR of $0.0015 \pm 0.0002\,\mathrm{mm}^{-1}$. Although the area of contact was very small, the onset temperature was lowered by 11°C, and the self-heat rates at 120, 135, and 150°C were higher compared with results using the Teflon coated thermocouple.

4.2.2. Nail test

A nail of carbon steel was added to each of two samples resulting in SVR values of 0.022 ± 0.002 and $0.024 \pm 0.002\,\mathrm{mm}^{-1}$ just prior to closing the sample cells at the beginning of an experiment. Because it was assumed in this study that glass and Teflon do not significantly participate in the HA decomposition reaction, a glass cell and a Teflon-coated sample thermocouple were used to ensure that the only significant catalytic material was the nail. The effect of a nail on the HA reaction is shown in Fig. 5, which displays the self-heat rate as a function of temperature for HA of both types in tests with and without a nail. The presence of the nail resulted in greatly lowered onset temperatures, from 133 to136 to below 50°C, increased self-heat rates, and increased maximum self-heat rates from no greater than 5 to 13°C/min (WO) and 31°C/min (W). These tests demonstrate that the decomposition reaction of HA with and without stabilizers is strongly catalyzed by carbon steel (primarily iron).

Following the tests, the sample and nail remains were visually inspected. HA with stabilizers had a very intense blue color and the nail had changed from gray to black, as shown

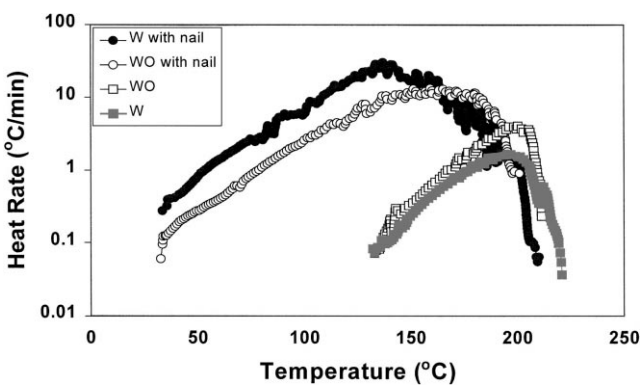

Fig. 5. Effect of carbon steel (nail) on the HA decomposition reaction in glass cells for W (with stabilizers) and WO (without stabilizers).

Table 4
Effect of test cell material on HA decomposition

Sample type	Cell material	Sample (g)	SVR[a] (mm^{-1})	T_o (°C)	$(\Delta T/\Delta t)_{max}$ (°C/min)	Liquid residue color	Solid residue color
W	Glass	2.21	NA	133	1.7	Bluish	Na[b]
W + nail	Glass	2.41	0.022	<50	31	Intense blue	Black[c]
W + inconel	Glass	2.26	0.0015	122	11	Bluish	Na[b]
W	SS	2.24	0.45	<50	9	Slightly blue	Reddish
W	Ti	2.23	0.45	<50	13	Intense blue	White
W	SS–Sa	2.20	0.45	<50	28	Yellowish	Gray
W	Ti–Sa	2.11	0.46	<50	9	Clear	White
WO	Glass	2.25	NA	136	4	Teal	Na[b]
WO + nail	Glass	2.25	0.024	<50	13	Slightly blue	Gray[c]
WO	SS	2.29	0.44	<50	71	Bluish	Reddish
WO	Ti	2.18	0.45	<50	100	Bluish	White
WO	SS–Sa	2.27	0.44	<50	17	Slightly blue	Yellowish
WO	Ti–Sa	2.28	0.44	<50	79	Clear	Greenish

[a] Ratio of metal surface contact area to sample volume.
[b] No residue observed.
[c] Nail color after the test. No residue was detected on the cell surface.

in Table 4. HA without stabilizers had a bluish color and there was no apparent difference in the nail color.

4.2.3. Tests in a stainless steel sample cell

The effect of a stainless steel sample cell on the HA decomposition reaction was measured in experiments with HA with and without stabilizers for a SVR of $0.45 \pm 0.01\,mm^{-1}$. As shown in Table 4 and Figs. 6 and 7, the HA with stabilizers exhibited a smaller maximum self-heat rate than the HA without stabilizers. This result is in contrast to the carbon steel nail test in which the HA with stabilizers exhibited the larger self-heat rate. The experimental

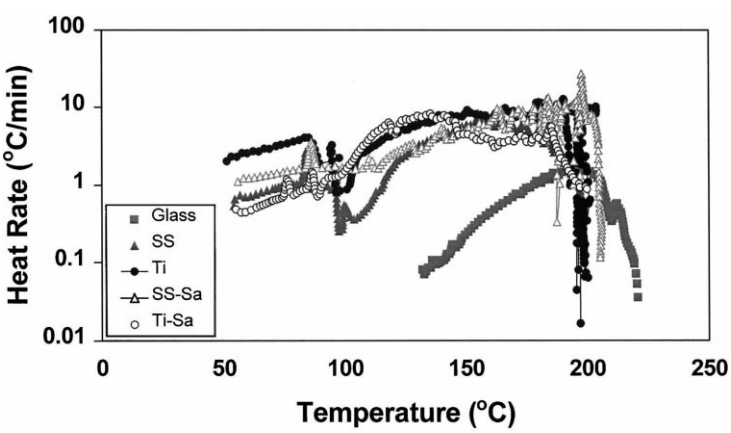

Fig. 6. Decomposition reaction of HA with stabilizers (W) in various test cell materials — Sa (coated with silica).

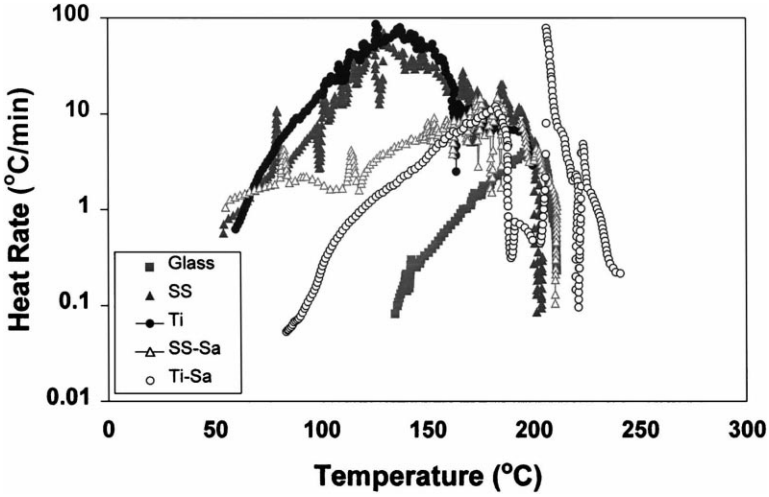

Fig. 7. Decomposition reaction of HA without stabilizers (WO) in various test cell materials — Sa (coated with silica).

reproducibility was lower in the SS and the other metal cell experiments, because a small change in sample weight changes the surface area of catalyst, which directly affects the reaction and self-heat rate. As listed in Table 4, the sample remains in the SS cell for HA with and without stabilizers were bluish in color, and a reddish residue was attached to the cell.

4.2.4. Tests in titanium sample cells

The onset temperatures and maximum self-heat rates of HA with stabilizers in three titanium sample cell tests with various sample sizes and ϕ factors are shown in Table 5. Because of the relatively large amounts of sample used in two of these experiments, the maximum self-heat rates generated by the decomposition reactions (1,907 and 943°C/min) were beyond the APTAC's capability to track the reactions in the adiabatic mode (adiabatic tracking for temperatures rises up to 400°C/min). Fig. 6 shows that HA with stabilizers in titanium sample cells exhibited a slightly greater self-heat rate than in stainless steel cells between 100–150°C. As seen in Table 4 and Fig. 7, the self-heat rates of HA without stabilizers in SS and Ti cells are similar. As listed in Table 4, the sample remains in the titanium cell for HA with and without stabilizers were bluish in color, and a white solid residue was observed on the cell surface.

Table 5
Effect of size for W samples in Ti cells

Sample (g)	$\sim\phi$	Onset temperature T_o (°C)	$(\Delta T/\Delta t)_{max}$ (°C/min)
2.23	3.6	<50	13
6.20	1.9	41	943
7.24	1.8	41	1907

4.2.5. Test in silica coated sample cells

In an attempt to provide a neutral environment in metal cells for the HA decomposition reaction, cells of Ti and SS were coated with silica (SiO_2) by chemical vapor deposition. The results of these experiments are summarized in Table 4 and in Figs. 6 and 7, where it is apparent that the sample cell surfaces were not fully pacified by the coating process. As shown in Fig. 7, the self-heat rates for sample without stabilizers were reduced but were still much greater than the rates in glass cells. For the HA industrial sample with stabilizers, shown in Fig. 6, no reduction in self-heat rate was observed. Fig. 6 shows also that HA with stabilizers in Ti–Sa sample cells exhibited a somewhat larger self-heat rate than in SS–Sa cells between 100–150°C. As shown in Fig. 7, the HA without stabilizers in a Ti–Sa cell exhibited two major exotherm peaks with maximum self-heat rates of 12 and 79°C/min. The sample remains in the silica coated cells for HA with and without stabilizers had varying appearances, which are listed in Table 4.

4.3. Exothermal activity above 200°C in metal cells

With the exception of HA without stabilizers in a Ti–Sa cell, all samples tested in metal cells exhibited major exothermic activity only below 200°C. From 200 to 300°C only small self-heat rates, generally <1°C/min, were observed in the sample sizes tested. The HA without stabilizers sample in a titanium cell exhibited a more energetic but still mild second exotherm with a maximum self-heat rate of 6°C/min in this temperature range. This mild exothermal activity from 200 to 300°C is not shown in Figs. 6 and 7.

5. Conclusions

In glass cells, HA decomposes exothermically with an onset temperature of ∼133–136°C, where onset temperature is defined as the temperature at which the self-heat rate of the sample is 0.05°C/min. The overall decomposition reaction was modeled with first-order kinetics with an activation energy of ∼29–34 kcal/mol. Stability tests for the industrial sample (HA with stabilizers) show that at 100°C the decomposition reaction generates ∼0.4 psi/h of vapor. A primary effect of the HA stabilizers in the industrial sample is to reduce the HA decomposition rate in neutral storage (plastic or glass) at temperatures near ambient and below. Because the HA decomposition products favor the overall decomposition reaction, the effect of these products is to lower the onset temperature and increase the reaction rate.

The HA decomposition reaction is enhanced by metals, which may catalyze the oxidation of intermediates such as ammonia. Inconel with a surface to sample volume of $0.0015\,mm^{-1}$ reduced the onset temperature of the industrial HA (with stabilizers) by 11°C, and a $0.022\,mm^{-1}$ surface to volume ratio of a carbon steel nail reduced the onset temperature to below 50°C and increased the self-heat rate of HA with stabilizers by a factor of ∼15. In both SS and Ti sample cells, the maximum self-heat rate of the HA with stabilizers was lowered by a factor of ∼8 compared to the HA without stabilizers. Silica coating did not pacify metal surfaces, and in all the tested metal cells, uncoated and coated with silica, the onset temperatures were less than 50°C for each of HA with and without stabilizers. Most of the exothermic activity for the sample sizes employed was below 200°C, but HA

without stabilizers in a Ti–Sa cell exhibited a second major exotherm above 200°C with a maximum self-heat rate of 79°C/min. These results demonstrate that HA decomposition in air and in contact with metal surfaces, uncoated or coated with silica, is a complex reacting system, and the decomposition products depend on the participating surfaces as suggested by the variety of liquid and solid residue colors listed in Table 4.

Prior to the accident that destroyed the Concept Sciences plant, the final step in their routine production of HA from hydroxylamine sulfate was vacuum distillation at 50°C, which is well below the temperatures for significant decomposition rates of HA in glass cells reported here. The presence of metal contaminants or significantly higher temperatures, however, can lead to greatly increased decomposition rates. Decomposition or reaction rate data and the effect of catalysts are essential for safe design, storage, use, and handling of potentially hazardous chemicals. Therefore, the availability of information such as described in this work, use of the information in industrial procedures, and training of plant personnel can help to promote the design of safe and economic processes employing these chemicals.

Additional research is necessary to determine the species involved in the HA decomposition reaction system and to study the effects of air. Only the fundamental understanding of this reaction will enable safe design and validation of strategies for safe storage, use, and handling of 50 wt.% hydroxylamine/water.

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