

# Thermal decomposition hazard evaluation of hydroxylamine nitrate

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## Abstract

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine family and it is a liquid propellant when combined with alkylammonium nitrate fuel in an aqueous solution. Low concentrations of HAN are used primarily in the nuclear industry as a reductant in nuclear material processing and for decontamination of equipment. Also, HAN has been involved in several incidents because of its instability and autocatalytic decomposition behavior.

This paper presents calorimetric measurement for the thermal decomposition of 24 mass% HAN/water. Gas phase enthalpy of formation of HAN is calculated using both semi-empirical methods with MOPAC and high-level quantum chemical methods of Gaussian 03. CHETAH is used to estimate the energy release potential of HAN. A Reactive System Screening Tool (RSST<sup>TM</sup>) and an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC<sup>TM</sup>) are used to characterize thermal decomposition of HAN and to provide guidance about safe conditions for handling and storing of HAN.

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*Keywords:* Hydroxylamine nitrate; APTAC; Screening methods; Autocatalytic reaction; Thermal decomposition

## 1. Introduction

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine family. High concentrations of HAN are used as liquid propellants, and low concentrations of HAN are used primarily in the nuclear industry for decontamination of equipment. Due to its instability and autocatalytic decomposition behavior, HAN has been involved in several incidents [1]. Therefore, the thermal stability and decomposition pathway of HAN in water are of interest. Several groups have investigated the kinetics and mechanism of HAN decomposition using various techniques and under different conditions [2–5]. However, due to its highly exothermic and rapid decomposition behavior, these studies could not provide complete information about the decomposition process. In this work, the thermal decomposition hazard of HAN is evaluated using both theoretical and experimental methods.

## 2. Theoretical screening methods and results

On May 14, 1997, an incident occurred in the Chemical Preparation Room of the Plutonium Reclamation Facility at the U.S. Department of Energy (DOE) Hanford's Plutonium Finishing Plant. The explosion destroyed the HAN storage tank and the room, and residual plutonium leaked from the building as wastewater [6]. During the investigation, it was determined that the root causes of the incident were inadequate hazard evaluation, inadequate auditing of safety management systems, and inadequate training of personnel on reactive hazards [7].

A systematic approach was proposed to evaluate reactive chemical hazards [8]. The first step of hazard evaluation is to use simple screening tools. For reactivity screening, Molecular Orbital Package (MOPAC) and ASTM Chemical Engineering Thermodynamics and Hazard Evaluation (CHETAH) are proven to be reliable and practical tools based on the analysis of the 167 incidents reported by Chemical Safety and Hazard Investigation Board (CSB) [9].

In this study, the semi-empirical quantum mechanical method MOPAC was employed to calculate the heat of for-

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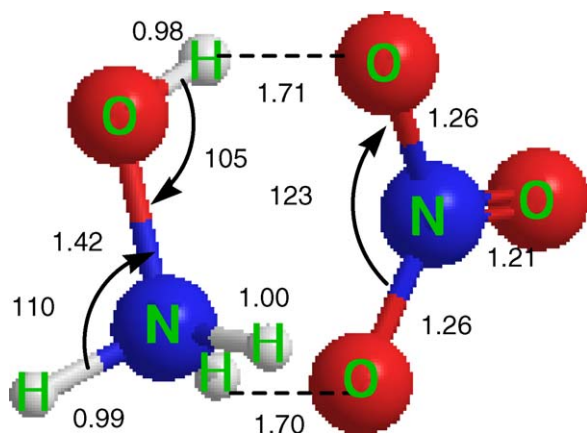
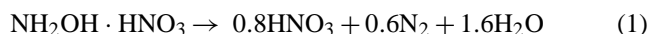


Fig. 1. The optimized gas phase structure of hydroxylamine nitrate.

mation of HAN at the level of theory of AM1 [10] and PM3 [11]. The optimized structure of gas phase HAN is shown in Fig. 1. The calculated gas phase heats of formation at 298 K are  $-64.8$  and  $-57.8$  kcal/mol using AM1 and PM3, respectively. In order to validate the results, the high level quantum mechanical method G2MP2 [12] from the Gaussian 03 suite of programs [13] was also used to calculate the heat of formation of HAN. The detailed method of calculating heat of formation is described in a Gaussian Whitepaper [14]. The obtained heat of formation of  $-61$  kcal/mol is about the average of the results using the AM1 and PM3 methods.

The energy release potential of HAN decomposition was evaluated by the ASTM CHETAH program, in which the gas phase heat of formation of  $-61$  kcal/mol was used as an input. The maximum heat of decomposition of HAN was estimated to be  $-57.1$  kcal/mol with the final products of nitrogen, nitric acid, and water, as shown in Eq. (1). CHETAH provided a hazard classification of MEDIUM, but the overall energy release potential is HIGH. Therefore, further experimental study is necessary for the hazard evaluation of HAN decomposition to measure the temperature and pressure profiles.



### 3. Experimental

#### 3.1. Sample

Hydroxylamine nitrate (24 mass% in water solution, Aldrich catalog number 438235) was used without further purification and analysis.

#### 3.2. Reactive System Screening Tool (RSST<sup>TM</sup>)

The RSST, manufactured by Fauske & Associates, is a calorimeter for rapid measurement of reaction thermal behav-

ior for temperatures up to  $400^\circ\text{C}$  and pressures up to 500 psig. An open, 10 ml sample cell typically made of glass is placed inside a pressure vessel (400 ml) that can withstand pressures up to 500 psig. The RSST can be used not only for screening the reactive chemicals, but also for designing emergency relief devices. In this paper, glass thermocouples and polymer coated magnetic stirrer bars were used to provide a metal-free environment for the reactions. A fixed heating rate of  $1^\circ\text{C}/\text{min}$  was used for temperatures up to  $400^\circ\text{C}$ . The shutdown pressure limit was 450 psig. Initial nitrogen pressures of 250 psig were used to reduce material loss from the sample cell.

#### 3.3. Automatic Pressure Tracking Adiabatic Calorimeter (APTAC<sup>TM</sup>)

Adiabatic calorimetry 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 close to the temperature of the sample. The APTAC calorimeter can be operated in a variety of test modes, such as Heat–Wait–Search, heat ramp, and isothermal aging with temperatures up to  $500^\circ\text{C}$  and pressures ranging from vacuum to 2000 psia, and it can track exotherms at heat generation rates from 0.04 to  $400^\circ\text{C}/\text{min}$ . 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. This allows use of a thin-wall sample cell which, when combined with the usual charge volume, can produce low thermal inertia data. For the present work, the measurements were conducted in glass sample cells of nominal 100 ml volume, which can provide a metal-free environment for the reactions, and also in titanium and stainless steel sample cells of nominal 130 and 50 ml volumes, respectively, to test the effect of metals on the thermal decomposition of HAN. Teflon coated thermocouples were used to prevent the contact of hydroxylamine solution with the metal thermocouple sheath.

The 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 more difficult to estimate the heat of the reaction from the experiment. Also, the liquid heat capacity of hydroxylamine nitrate is absent in the literature. However, because water was the solvent and a major product in this experiment, the heat capacity of liquid water ( $1 \text{ cal}/(\text{g}^\circ\text{C})$ ) was used to estimate the thermal inertia ( $\phi = (M_s C_s + M_b C_b)/M_s C_s$ , where  $M$  is the mass,  $C$  is the heat capacity and subscripts b and s refer to the sample bomb and the sample, respectively) and heat of reaction from the APTAC experimental results.

### 3.4. Experimental methods

The APTAC Heat–Wait–Search (HSS) mode was used: the sample was heated at 2 °C/min to a starting temperature, and the temperature was allowed to stabilize for 25 min, following which the APTAC searched 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 (0.05 °C/min), the apparatus tracked the reaction adiabatically until the reaction ended or one of the shutdown criteria was met. If no exotherm was detected, the apparatus heated the sample to the next search temperature and the steps repeated until one of the shutdown criteria was met. The onset temperature is defined as the temperature at which an exotherm is detected, and it is usually the lowest temperature at which the sample self-heat rate surpasses the preset threshold (0.05 °C/min) in the ‘search’ or ‘adiabatic’ mode.

The APTAC Heat–Soak–Search mode was also used: the sample was heated to a specified soak temperature and held adiabatically. Every 60 min or if the sample temperature rose 1 °C above the soak temperature, the self-heating rate would be polled and compared with a pre-defined sensitivity threshold. If the self-heating rate exceeded the threshold, a runaway reaction was detected and the sample was kept adiabatically. If the self-heating rate was less than the threshold, the sample would be cooled back to the soak temperature. The steps continued for a defined period. If it failed to detect self-heating at the end of the soak period, the system would proceed with a standard Heat–Wait–Search mode. The HSS method is generally used to test the effectiveness of inhibitors added to the reactants. In this study, the HSS method was employed to study the effect of autocatalysis on the decomposition of HAN. The autocatalytic product species is generated during the soak period and thus allows the reaction eventually to runaway in an adiabatic system when its concentration reaches a certain level. An appropriate soak time and temperature are chosen based on the knowledge of the reactive system.

For the glass sample cell, the maximum allowable pressure imbalance is 150 psi. Due to the extremely rapid exothermic reactivity of hydroxylamine nitrate solution, it is difficult for the APTAC to track pressure rise fast enough. The pressure imbalance was above 100 psi even when small samples (about 4 g) were used in these tests. Stirring was not necessary because of the small sample size.

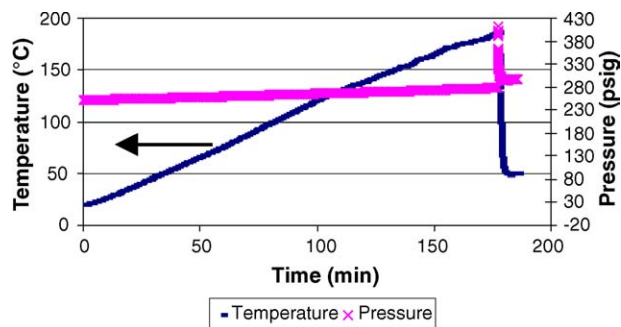


Fig. 2. RSST experimental results of the thermal decomposition of HAN.

## 4. Results and discussions

### 4.1. RSST experimental results

The RSST experimental results are shown in Fig. 2. At the temperature of 180 °C, the pressure increases dramatically, but the temperature profile does not show increase like a typical exothermic runaway reaction. From the results, the decomposition becomes measurable around 180 °C. The absence of a temperature increase can be attributed either to an endothermic reaction or to the expulsion of the thermocouple. The reaction starts very rapidly and the generated vapor and gas products can blow the thermocouple out of the sample cell into the pressure containment vessel. The temperature of the containment vessel is much lower than that of the sample cell because only the sample cell is heated by a bottom heater that surrounds it. In addition, the glass sample cells were broken into pieces during testing, probably because of the violent decomposition. In order to obtain a complete temperature profile, a closed cell experiment is necessary, and the APTAC is an ideal apparatus for this task.

### 4.2. Effect of materials of construction

The APTAC HWS mode was employed to determine the overall decomposition behavior of hydroxylamine nitrate, such as onset temperature ( $T_0$ ), maximum temperature ( $T_{max}$ ), and maximum pressure ( $P_{max}$ ). The experimental results for glass, titanium, and stainless steel sample cells are presented in Table 1 and Figs. 3 and 4. The experiments confirm the expectation that the reaction is exothermic and reveal that RSST temperature profile is caused by the expulsion of the thermocouple due to the rapid pressure increase.

Table 1  
APTAC Heat–Wait–Search results of HAN thermal decomposition

HAN 4.2 g	$T_0$ (°C)	$T_{max}$ (°C)	$P_{max}$ (psia)	$dT/dt_0$ (°C/min)	$dT/dt_{max}$ (°C/min)	$dP/dt_{max}$ (psi/min)	Non-condensable (psia) (50 °C)	Phi factor ( $\phi$ )	$\Delta H_{rxn}$ (kcal/mol)
Glass cell	171	196	296	0.07	416	174	41	3.3	33
Ti cell	150	179	194	0.06	279	28	26	2.0	23
SS cell	139	169	227	0.06	179	294	55	3.6	43

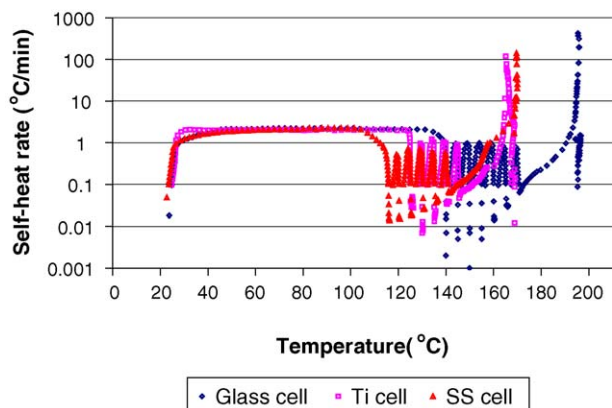


Fig. 3. Effect of materials of construction of sample cells on the self-heat rate vs. temperature profiles of HAN decomposition.

The effect of sample cell material on onset temperature shows that a glass cell provides a metal-free environment, and metals such as titanium and stainless steel can accelerate the decomposition of hydroxylamine nitrate. Compared with glass, titanium initiates the decomposition at a lower temperature, but less heat is evolved from the reaction, while stainless steel can cause a decomposition with more heat release.

#### 4.3. Comparison of gas phase and liquid phase temperatures

The Teflon coated thermocouple was located as close to the bottom of the sample cell as possible to measure liquid temperature. A stainless steel sheath thermocouple with a diameter of 0.02 in. was placed inside the neck of the sample cell to detect gas phase temperature. The gas and liquid temperatures of the HAN decomposition in a stainless steel cell are compared in Fig. 5. The temperatures are very close until the fast propagating reaction (explosion) occurs around 160 °C. The gas phase jumps to a maximum temperature of 185 °C, and then cools down. The gap of 25 °C in data points in the gas phase between the start of explosion and the maximum temperature may be due to slow sampling of data points by the APTAC. Meanwhile, the liquid tempera-

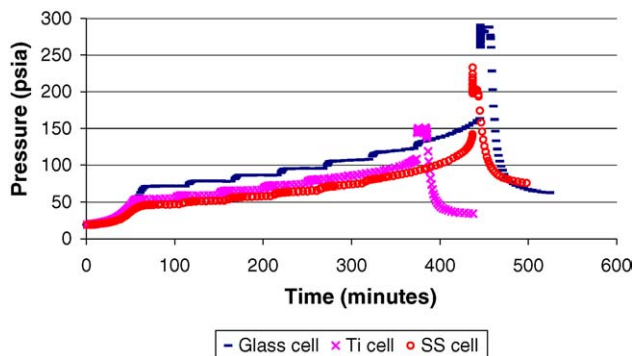


Fig. 4. Effect of materials of construction of sample cells on the pressure profiles of HAN decomposition.

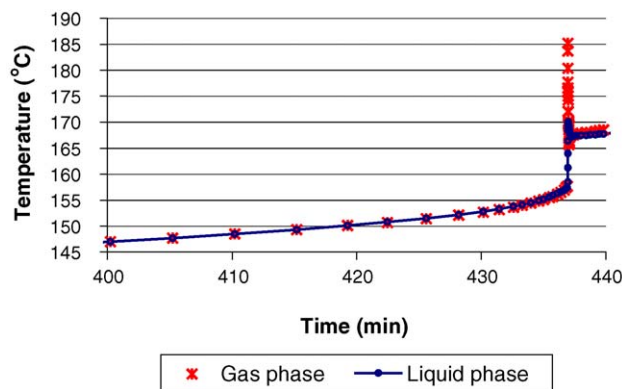


Fig. 5. Comparison of the gas phase and liquid phase APTAC temperature profiles for HAN decomposition in a stainless steel cell.

ture keeps increasing to a maximum temperature of 170 °C, which is much lower than the gas phase maximum temperature. It is most likely that the explosion starts in the gas phase due to the effect of the stainless steel thermocouple sheath, and then the released heat transfers to the liquid phase.

#### 4.4. Autocatalytic decomposition

Previous studies showed that hydroxylamine decomposition is well-described by a first order kinetics with an overall activation energy of 29 kcal/mol [15]. The decomposition curve of 24 mass% hydroxylamine nitrate/water is compared with that of 50 mass% hydroxylamine/water in Fig. 6. Hydroxylamine nitrate decomposition starts at 170 °C and the temperature increases slowly until 180 °C, at which point the temperature suddenly increases very rapidly to a maximum temperature of 196 °C. The temperature curve of hydroxylamine nitrate appears to consist of two stages: a slow initiation stage followed by a fast explosion stage. These two stages form a sharp corner. In contrast, for the decomposition of hydroxylamine, the temperature increase starts immediately at the onset temperature and smoothly curves up to the maximum temperature. From comparison of the decomposition temperature curves, it can be concluded that hydroxylamine nitrate decomposition is an autocatalytic reaction. Initially the decomposition shows only little heat release, and therefore the temperature increase is slow. After an induc-

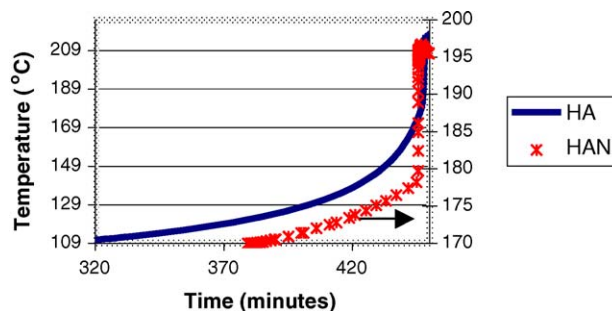


Fig. 6. Comparison of the APTAC decomposition curve of hydroxylamine nitrate with hydroxylamine in glass cells.

Table 2  
APTAC Heat–Soak–Search results of HAN thermal decomposition

HAN 4.2 g	Soak temperature (°C)	$T_0$ (°C)	$T_{\max}$ (°C)	$P_{\max}$ (psia)	$dT/dt_0$ (°C/min)	$dT/dt_{\max}$ (°C/min)	$dP/dt_{\max}$ (psi/min)	Non-condensable (psia) (50 °C)	Phi factor ( $\phi$ )	$\Delta H_{\text{rxn}}$ (kcal/mol)
Glass cell	150	165	184	233	0.07	344	111	41	3.3	25
Ti cell	130	131	143	103	0.05	128	12	24	2.0	10
SS cell <sup>a</sup>	120	127	140	137	0.07	139	6	53	3.6	18

<sup>a</sup> Results for the second exothermic peak were shown.

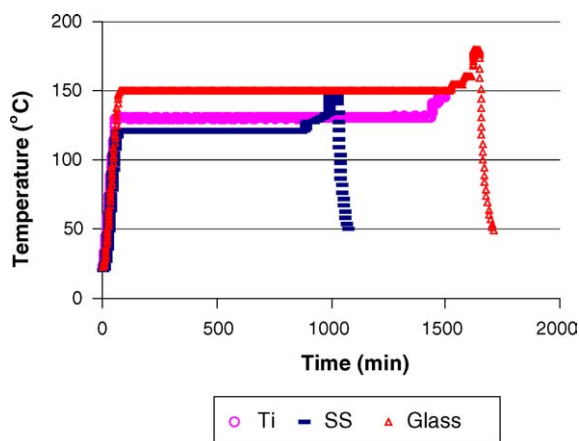


Fig. 7. Temperature profiles of HSS experimental results of hydroxylamine nitrate.

tion period, the concentration of the autocatalytic product reaches a threshold level and the reaction rate becomes very rapid.

In order to test the aging effect on the thermal decomposition of hydroxylamine nitrate, the HSS method was employed. The experimental results using glass, titanium, and stainless steel sample cells are presented in Table 2 and Figs. 7 and 8. The soak temperatures were chosen as 20°C lower than the onset temperatures of the HWS results, and the soak period was 24 h. During the soak and search periods, although the temperature is almost constant, a pressure increase is detected because the decomposition is occurring at

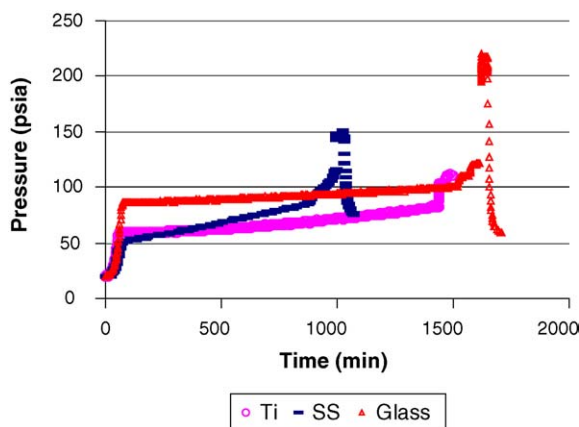


Fig. 8. Pressure profiles of HSS experimental results of hydroxylamine nitrate.

a low self-heat rate. In the glass cell, significant self-heat rates were not detected during the soak period, so the apparatus proceeded with the HWS mode. In the titanium cell, a significant decomposition was detected during the soak period, and a fast explosion occurred at the end of the 24-h soak period. In the stainless steel cell, two exothermic peaks were detected. One small peak was detected during the soak period and another one at higher temperature.

The detected onset temperatures in the HSS mode were lower than those of the HWS mode alone. Besides the onset temperatures, the maximum self-heat rates and maximum pressure rates were also lower in Table 2 than the ones in Table 1. During the soak and search periods, the initiation reaction starts and the autocatalytic product is generated. If the self-heat rate is not sufficient, the temperature will be reduced to the soak temperature. Therefore, some heat loss can occur during the soak period, and the estimated heats of reaction are reduced significantly in the HSS mode.

The self-heat rates of the HWS and HSS modes in a stainless steel cell are compared in Fig. 9. The upward curves at high temperatures essentially appear as vertical lines, reflecting a rapid propagating reaction, and the corresponding self-heat rate points seem like vertical lines because the propagation of the reaction is very fast. Because of the 24 h aging, the temperature corresponding to the maximum self-heat rate is 25 degrees lower in the HSS mode than that in the HWS mode. The explosion can occur at a significantly lower temperature because a significant amount of autocatalytic product is accumulated during the soaking period. This autocatalytic decomposition behavior poses a challenge for long-term storage of such reactive chemicals.

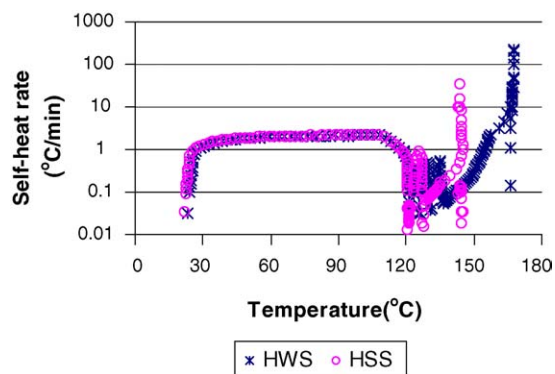


Fig. 9. Comparison of HWS and HSS experimental results of HAN in a stainless steel cell.

## 5. Conclusions

The thermal decomposition hazard of 24 mass% hydroxylamine nitrate/water was evaluated using calorimetric methods. Screening tools predict the hazard of possible heat release and pressure generation. The temperature curve of the APTAC measurements shows two stages: a slow initiation stage and a fast propagating stage. The explosion stage occurs very suddenly and quickly. By comparing the HWS and HSS experimental results, the decomposition exhibits a strong autocatalytic behavior, and the explosion stage can start at a much lower temperature following a certain aging period. Stainless steel and titanium can accelerate the decomposition at lower temperatures compared to glass. Based on our study, HAN must be handled at low temperatures, and long-term storage should be avoided because of its autocatalytic decomposition behavior.

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## References

- [1] Technical Report on Hydroxylamine Nitrate, US Department of Energy, 1998.
- [2] C.A.V. Dijk, R.G. Priest, Thermal decomposition of hydroxylammonium nitrate at kilobar pressure, *Combust. Flame* 57 (1984) 15–24.
- [3] V.A. Rafeev, Y.I. Rubtsov, Kinetics and mechanism of thermal decomposition of hydroxylammonium nitrate, *Russ. Chem. Bull.* 42 (11) (1993) 1811–1815.
- [4] J.W. Schoppelrei, T.B. Brill, Spectroscopy of hydrothermal reactions. Part 7. Kinetics of aqueous  $[\text{NH}_3\text{OH}]\text{NO}_3$  at 463–523 K and 27.5 MPa by infrared spectroscopy, *J. Phys. Chem. A* 101 (1997) 8593–8596.
- [5] J.C. Oxley, K.R. Brower, Thermal decomposition of hydroxylamine nitrate, *Proc. SPIE Int. Soc. Opt. Eng.* 872 (1988) 63–70.
- [6] Peña visits “most dangerous place on Earth”, in CNN, August 27, 1997.
- [7] Hazard Investigation: Improving Reactive Hazard Management, US Chemical Safety and Hazard Investigation Board (editor), 2002.
- [8] M.S. Mannan, W.J. Rogers, A.A. Aldeeb, A systematic approach to reactive chemicals analysis, in: *Proceedings of HAZARDS XVI*, Manchester, United Kingdom, November 6–8, 2001.
- [9] C. Wei, W.J. Rogers, M.S. Mannan, Application of screening tools in the prevention of reactive chemical incidents, *J. Loss Prev. Process Ind.* 17 (4) (2004) 261–269.
- [10] M.J.S. Dewar, E. Zebisch, E.F. Healy, J.J.P. Stewart, Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model, *J. Am. Chem. Soc.* 107 (13) (1985) 3902–3909.
- [11] J.J.P. Stewart, Optimization of parameters for semiempirical methods. I. Method, *J. Comput. Chem.* 10 (2) (1989) 209–220.
- [12] L.A. Curtiss, K. Raghavachari, J.A. Pople, Gaussian-2 theory using reduced Møller–Plesset orders, *J. Chem. Phys.* 98 (2) (1993) 1293–1298.
- [13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Menonucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh, PA, 2003 (revision B. 04).
- [14] Ochterski, J.W., Thermochemistry in Gaussian, [http://gaussian.com/g\\_whitepap/thermo.htm](http://gaussian.com/g_whitepap/thermo.htm), 2000.
- [15] 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.