

Thermal stability of chemicals under fire conditions: the case of hydroxylamine sulphate

Danzi E.¹, Marmo L.¹, G. Pio², E. Salzano²

¹ Politecnico di Torino, Torino, Italy

² Department of Civil, Chemical, Environmental, and Materials Engineering – DICAM, Alma Mater Studiorum - University of Bologna, Bologna, Italy

1 Introduction

The owners of chemical warehouses and plants, where large amount of hazardous chemicals are present, must deal with fire and explosion safety. To this aim, either prevention or mitigation systems must be adopted. Both can operate passively or actively. Passive actions are often obtained by the physical separation of materials, as compartmentation or fire-resistant walls. In the case of explosion hazards, large venting area by loosely hinged doors, large windows or light roofs are usually adopted. Active systems include sprinklers, water mist, water curtains, inerting agent injection, and others. Both prevention and mitigation systems must be designed according to the hazard of the stored substances. For to the UN-based GHS (the Globally Harmonized System of Classification and Labelling of Chemicals), implemented in Europe in 2008 by CLP Regulation (CLP, 2008) on the classification, labelling and packaging of substances and mixtures, chemical substances are classified by use of the H (hazards) and P (precautionary) statements, which indicate the primary nature of hazards. Indeed, any substance to be placed on the market must be classified by using existing information (Annex VI of CLP) or by using a self-classification based on available data or calculation, starting from ingredients and their concentrations in the case of mixtures. Quite often, however, no GHS indications are given in the case of fire conditions, i.e. for the escalation effects produced by heat radiation on solid or liquid chemicals.

In this work, the case of hydroxylamine sulphate $(\text{NH}_3\text{OH})_2\text{SO}_4$, which has been recently responsible for a large-scale explosion in a chemical warehouse (described in Salzano et al. 2018), is analysed. This substance is largely used as intermediate in the production of caprolactam, but also in pharmaceutical, food and textile industry (EU Risk Assessment Report, 2008). The substance is relatively stable at ambient temperature. Accordingly, GHS and CLP (1272/2008) do not consider fire or explosion hazards. Both hydroxylamine sulphate and hydroxylamine (50% water solution) are indicated as corrosive, harmful, capable of health and environmental hazards (GHS05, 07, 08 and 09), but no fire & explosion hazard is taken into account by CLP. However, the classification of EU Directives 67/548/EEC and 1999/45/CE, recognised $(\text{NH}_3\text{OH})_2\text{SO}_4$ as R2 i.e.: “risk of explosion by shock, friction, fire, or other sources of ignition”. This derives directly from the definition: the 1967 Directive classify as explosive any substance or preparation which may react exothermically without atmospheric oxygen thereby quickly evolving gases, and which, under defined test conditions, detonate, quickly deflagrate or explode due to heating when partially confined. Besides, the 1999 Directive reports that substances and preparations, which may explode under the effect of flame or which are more sensitive to shock or friction than dinitrobenzene, should be classified as explosive, accordingly. It is quite evident that, in both cases, domino effects

due to fire conditions were taken into consideration and that this information are somehow neglected if only new harmonised rules are considered, although material safety data sheets are sufficiently detailed.

The severity of the issue rises if these substances must be handled and stored, as labelling is relevant to manage with them adequately and safely. According to GHS, operators have no indications regarding possible hazardous behaviour of hydroxylamine sulphate, if stored improperly. The only indication came from the previous Directive, which defined it as explosive (R2), but this classification is being removed from data sheets. Transportation information (in MSDS, Section 14) only alerts about the corrosive nature of the substance, defining it equals to 8, i.e. corrosive, as in Commission économique pour l'Europe (2018). Coherently with its explosive behaviour in fire conditions, hydroxylamine sulphate should be labelled as 4.1a, which indicates “Other explosive substances”. Alongside this, joint storage is also an issue, when two incompatible substances are kept close by and without any fire resistance rated separations. According to joint storage matrix, (see Table 1) substances labelled as 4.1a must be stored separately from toxic, radioactive and oxidising agents (red cells in Table 2), while extreme care has to be paid in joint storage with combustible solids and liquids (yellow cells), where note “1” means restrictions, i.e. storage could be allowed only after a risk assessment analysis is performed to prevent the risk.

Table 1: Joint storage of 4.1a substance (as hydroxylamine sulphate) with others, extracted from TRGS-510 (2013).

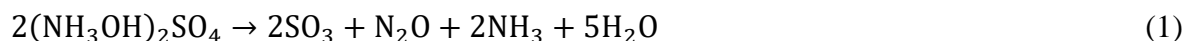
Classification	10-13	13	12	11	10	8b	8a	7	6.2	6.1d	6.1c	6.1b	6.1a
4.1a	1	1	1	1	1	1	1						

Table 2: continues

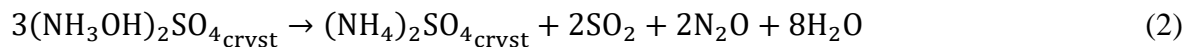
	5.2	5.1c	5.1b	5.1a	4.2	4.1b	4.1a
4.1a	1					1	1

2. The explosive behaviour of $(\text{NH}_3\text{OH})_2\text{SO}_4$

According to GHS and CLP (1272/2008), no “explosive” definition is due to $(\text{NH}_3\text{OH})_2\text{SO}_4$ although several evidences show that at temperatures just above 120°C the substance decomposes “explosion likely” (EU, 2008). Indeed, at lower temperatures, $(\text{NH}_3\text{OH})_2\text{SO}_4$ degrades exothermally, thus generating sulphur trioxide (SO_3), nitrogen oxides (NO_x), ammonia (NH_3) and water according to the following reaction:



or alternatively (Shidlovskiy, 1962):



This reaction is entropically explosive, due to the higher number of moles produced by the decomposition. Furthermore, the complex mixture of products may undergo to further reactions with air.

At higher temperature, the solid substance $(\text{NH}_3\text{OH})_2\text{SO}_4$ is more unstable. More specifically, it degrades explosively at 170 °C with a complex reaction system, which is still under definition. The first reaction is likely to be the exothermic decomposition to sulfuric acid (H_2SO_4) and hydroxylamine (NH_2OH), a reaction which is also affected when exposed to carbon dioxide and moist air. Sulphuric acid derives from the hydration of sulphur trioxide: a clear evidence of this reaction has been witnessed during the investigation of a recent accident in Italy, described in Salzano et al. (2018). Here a firefighter identified a “yellowish” fluid leaking outside the warehouse, where hydroxylamine sulphate was stored: this fluid was likely *oleum*, a mixture of SO_3 and H_2SO_4 .

The exothermic degradation occurs at the melting point (170°C), which is the reason for the temperature threshold given above. The produced NH_2OH is then responsible for a dual explosion: one is related to the explosive decomposition (in acid conditions due to the presence of the SO_3 , H_2SO_4 , and water) and the second is related to the oxidation of NH_2OH with air:



Eventually, under fire conditions, NH_2OH is formed. This substance is a well-known unstable and hazardous chemical. Some destructive episodes of explosion related to presence of hydroxylamine are indeed reported among recent cases by the US Chemical Safety and Hazard Investigation Board (CSB, 2002). NH_2OH is classified as H200 (unstable explosive), it should not be used as a pure substance and must be stored and manipulated in water solution in common industrial use. Even in these conditions, however, it behaves similarly to traditional explosives such as TNT although it has never been fully demonstrated to detonate.

2.1 Estimate of Hydroxylamine sulphate amount of case study (Salzano et al. 2018)

The damage analysis of the accident reported was reproduced according to ConWep® code of US Army (2002), for the cratering, the spalling and the breaching of the reinforced concrete structures of the warehouse involved. From these data the TNT mass capable of recreate the observed depression was estimated, and then the hydroxylamine amount, applying TNT equivalent ratio.

Table 1: Spalling and breaching limit values with respect to distance of target (columns) and explosive mass for main crater

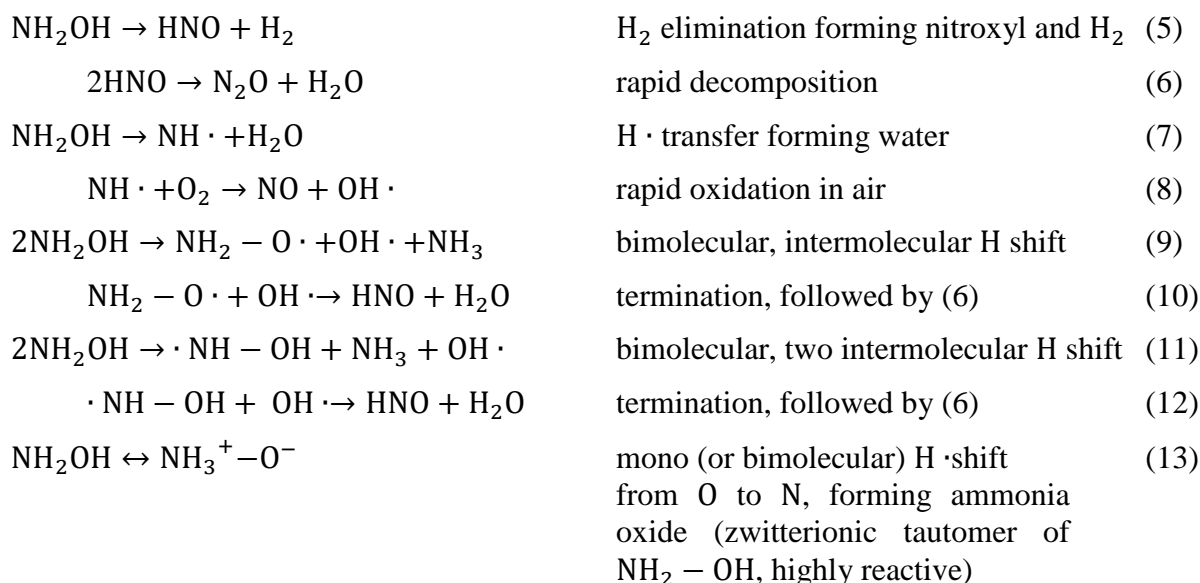
Explosive amount, TNT (kg)	40 kg		
Distance (m)	3	5	10
Spall (cm)	28.88	12.03	3.48
Breach (cm)	24.78	17.33	10.25

Table 2: Estimate of explosive amount capable of generating main crater, from ConWep simulation.

Explosive	ΔH_d (J/g)	m_{ex} (kg)
TNT	4184	40.0
Hydroxylamine sulfate	1818	92.0

3. Results

Most of the analysis of the NH_2OH are necessarily conducted in water solution, due to the intrinsic hazards (Adamopoulou et al., 2013). However, this substance could be likely found in gas phase when high temperature decomposition of $(NH_2OH)_2SO_4$ is of concern. A theoretical ab initio study of the gas decomposition has been presented (Wei, 2005). The possible (simplified) reaction paths are:



The heat of combustion and the Gibbs free energy variation with respect to the temperature for the NH_2OH decomposition and oxidation with air, in the gas phase, are shown in Figure 1.

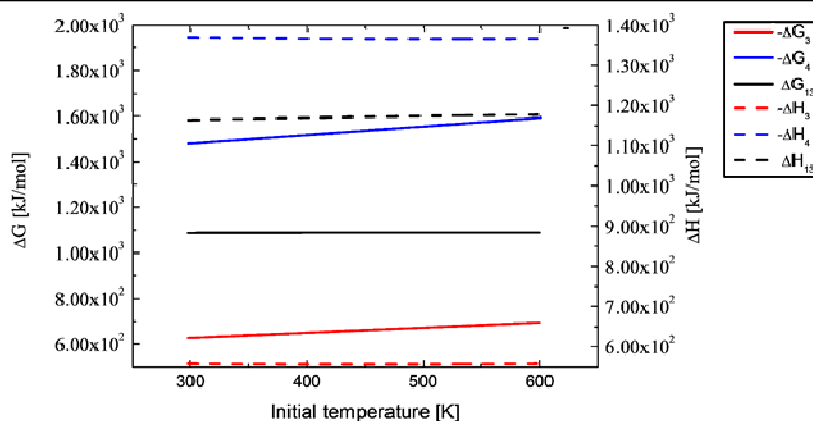


Figure 3: Enthalpy ΔH and Gibbs free energy ΔG variation with temperature for the decomposition and the combustion of hydroxylamine.

Both overall reactions 3 and 4 (the decomposition and the oxidation of NH_2OH) are spontaneous and exothermic, but the effect of temperature is relatively negligible and only slightly more favoured at higher temperature. The energy developed by the combustion is consistently higher than the energy of the decomposition reaction. It is worth noting the high energy developed by reaction 13, which produces $\text{NH}_3^+ - \text{O}^-$, thus confirming the hypothesis of some authors that the explosion behaviour for the decomposition reaction can be ascribed to the ammonia oxide reactivity.

4. Conclusions

The use of classification and labelling adopted by GHS alone is not self-consistent for any hazard classification. The material safety data sheet and other detailed information are necessary.

The behaviour of $(\text{NH}_3\text{OH})_2\text{SO}_4$ is complex and no heating due to fire must occur in warehouses or other storages. The confinement of this substance by compartmentation, similarly to solid peroxides, should be strongly advised.

When heated to lower temperature (130 °C), the formation of NH_2OH is possibly negligible. At the melting point (170 °C), the same substance is formed. The decomposition products include however the highly reactive $\text{NH}_3^+ - \text{O}^-$, which is likely to be responsible of the detonative potential observed in recent accidents (Salzano et al., 2018), where the most severe damage in the event were ascribed to hydroxylamine sulphate explosive decomposition. An estimate of the maximum mass of it capable of this damage entity is about 100 kg. Furthermore, the energy of decomposition of hydroxylamine sulphate is dramatically higher than the energy combustion of NH_2OH .

The analysis of the explosion characteristic of NH_2OH is still under investigation in the gas phase under fire conditions, i.e. in the presence of soot, CO and CO_2 . Further insights and investigations based on computational chemistry, due to the high hazard of this substance, will be considered in the next future.

Acknowledgments

This paper is dedicated to the memory of dr. Sam M. Mannam.

References

- Adamopoulou T., Papadaki Maria I., Kounalakis M., Vazquez-Carretero V., Pineda-Solano V., Wang Q., Mannan M.S., 2013. Thermal decomposition of hydroxylamine: Isoperibolic calorimetric measurements at different conditions, *Journal of Hazardous Materials*, 254– 255, 382– 389.
- CLP (2008). Regulation on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. European Union and Council.
- Commission économique pour l'Europe, Comité des transports intérieurs (2018). *Accord Européen relatif au transport international des marchandises dangereuses par route (ADR)*. ECE/TRANS/275 Vol.1. Nations Unies, New York et Genève.
- CSB (2002). U.S. Chemical Safety and Hazard Investigation Board, The Explosion at Concept Sciences: Hazards of Hydroxylamine, Washington, DC.
- EU Risk Assessment Report (2008). Bis(Hydroxylammonium)Sulphate, CAS No: 10039-54-0, EINECS No: 233-118-8, European Union, May 2008.
- Salzano, E., Debernardi, M.L., Riccio, D., Danzi, E., Marmo, L. (2018). A Case Study of Multiple Explosions of Chemicals Under Fire Conditions, 12th International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions (ISHPMIE), 13 17 August, Kansas City (OK), USA.
- Shidlovskiy, A.A. (1962). Combustion of the inorganic salts ammonium iodate and hydroxylamine sulfate, *Zhurnal Prikladnoy Khimii*, 35, 511-516.
- TRGS-510 (2013). Storage of hazardous substances in non-stationary containers. German Federal Institute for Occupational Safety and Health.
- United States Army Corps of Engineers (2002) Protective Design Center, Conwep® Conventional Weapon Effects.
- Wei C. (2005). Thermal runaway reaction hazard and decomposition mechanism of hydroxylamine system, PhD thesis, Texas A&M.