Reaction pathways of hydroxylamine decomposition in the presence of acid/base

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Abstract

Understanding reactivity and determining reaction pathways are important for the design and safe operation of industrial processes. In order to understand reaction mechanism, various experimental techniques were employed traditionally. However, with the development of computational tools, molecular modeling based on quantum chemical calculations has become a reliable approach to supplement experimental methods. The structures and energetics of reactants, products, intermediates and transition states can be calculated using quantum chemical methods. The thermodynamic and kinetic information can be used to elucidate the favorable reaction pathway. This paper presents the runaway reaction pathways developed by using both experimental and computational techniques. To illustrate the combined experimental and theoretical approach, hydroxylamine as an important industrial compound is used as an example case.

Hydroxylamine has been involved in two incidents since 1999 because of its thermal instability and incompatibility. In this study, thermal runaway reactions of hydroxylamine with various concentrations of KOH, HCl, and KCl were studied using a reactive system screening tool (RSST) and an automatic pressure tracking adiabatic calorimeter (APTAC). The thermokinetic data, such as onset temperature, heat of reaction, maximum self-heat rate, maximum pressure rate, and non-condensable gas pressure, were compared with those of hydroxylamine solution without added impurity. Our experimental study shows that the thermal decomposition behavior of hydroxylamine is affected by the presence of acid or base. Different decomposition pathways can be initiated by hydrogen and hydroxide ions. Hydrogen ion can increase the maximum self-heat and pressure rates while hydroxide ion can decrease the onset temperature and generate more gas products.

The decomposition mechanisms of hydroxylamine in alkaline and acidic solutions are proposed based on the final products, quantum mechanical calculations, and information from the literature. Enthalpies of reaction for elementary steps are calculated in both gas phase and liquid phase using GAUSSIAN 03 [1]. In the literature, HA free base decomposition at high temperatures was analyzed to occur according to Equations 1 and 2 under alkaline and acidic conditions, respectively [2]. Our proposed mechanisms fit the overall equations 1 and 2. The geometries of reactant, intermediates, and products are optimized using B3LYP/cc-pVDZ level of theory. The energies are further calculated using higher level of theories, as listed in Table 1.

$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O \qquad (1)$$
$$4NH_2OH \rightarrow N_2O + 2NH_3 + 3H_2O \qquad (2)$$

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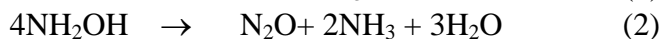
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The proposed reaction mechanisms can be used to give a reasonable explanation of the experimental results. The measured onset temperature decreases with the increasing pH because the reaction rate of initiation reaction will increase and more heat will be released with increasing concentration of hydroxide ions. Applying steady-state assumption on all the intermediates, the concentration of HNO is proportional to that of hydroxide ions. So, the ratio of the branching reaction will also increase with pH, more NH_2O radicals will be produced, and therefore, more heat will be generated, and more nitrogen will be produced with the increasing concentration of hydroxide ions.

NH(triplet) is more reactive than HNO with hydroxylamine and it plays an important role in the branching reaction. Once the decomposition is initiated in acid solutions, NH(triplet) is produced and the branching reaction begins with heat-release, while in alkaline solutions, the branching reaction is less exothermic. The difference of the branching reactions in the two cases may explain why the maximum self-heat rate and pressure rate were higher in acid solutions than in alkaline solutions.

Table 1. Comparison of enthalpies of reaction for elementary steps of hydroxylamine decomposition in alkaline/acidic solutions using different levels of theories. PCM model was used to carry out calculations in water solution.

ΔH_{rxn} (kcal/mol)	B3LYP/cc-pVDZ		G2		CCSD/cc-pVDZ		CBS-Q	
Base effect	Gas phase	Solution	Gas phase	Solution	Gas phase	Solution	Gas phase	Solution
$HA+OH^- \rightarrow NH_2O^- + H_2O$	-22.0	-11.6	-4.2	0.8	-19.1	-10.5	-5.0	-0.1
$NH_2O^-+ HA \rightarrow NH_2NHOH+OH^-$	2.4	-10.5	-19.0	-27.0	-1.7	-13.1	-18.3	-26.2
$NH_2NHOH \rightarrow HNO+NH3$	3.5	6.9	0.3	4.6	-3.0	0.7	0.9	5.5
$HNO+HA \rightarrow NH_2O+NH_2O$	4.3	0.4	18.4	13.0	16.7	12.8	15.1	9.2
$NH_2O+NH_2O \rightarrow N_2+2H_2O$	-116	-113.9	-147.2	-143.4	-142.8	-140.5	-144.2	-140.4
Acid effect								
$NH_3OH^+ \rightarrow NH+H_3O^+$	68.8	60.3	69.5	61.3	56.8	48.2	69.4	61.3
$H_3O^+ + HA \rightarrow NH_3OH^+ + H_2O$	-27.4	0.0	-30.6	0.0	-27.8	0.0	-30.7	0.0
$NH+HA \rightarrow NH_2+NH_2O$	-20.7	-21.4	-14.4	-15.8	-10.3	-11.0	-15.7	-17.3
$NH_2O+HA \rightarrow NH_2NHOH+OH$	21.7	19.8	17.1	23.1	13.8	11.8	18.4	16.9
$OH+HA \rightarrow NH_2O+H_2O$	-41.3	-41.9	-40.3	-49.3	-34.7	-35.3	-41.6	-43.2
$NH_2NHOH \rightarrow HNO+NH_3$	3.5	6.9	0.3	4.6	-3.0	0.7	0.9	5.5
$NH_2O+NH_2 \rightarrow HNO+NH_3$	-36.9	-32.3	-47.4	-41.7	-42.5	-37.9	-45.3	-39.2
$HNO+HNO \rightarrow N_2O+H_2O$	-84.2	-83.3	-86.9	-86.0	-77.8	-77.3	-88.9	-88.8
Other possible initiation steps								
$HA \rightarrow NH_2+OH$	62.0	59.0	64.8	69.4	53.4	50.4	64.6	61.6
$HA \rightarrow NH_2^+ + OH^-$	355.5	183.2	307.1	140.9	343.7	171.7	310.0	143.3

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