Plasma Chemistry of Partially Ionized Hydroxylammonium Nitrate: Interactions with H_2O, NO, and NO_2 Ions

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Abstract: Ionic liquids are one class of propellants being investigated for use in dual-mode spacecraft propulsion systems. Hydroxylammonium Nitrate (HAN) is the ionic liquid of interest in this study. Its chemistry and decomposition have been thoroughly investigated; however, the chemistry of partially ionized HAN is not well understood. Ab-initio modelling is used to determine the chemistry of ion-neutral reactions between NH_2OH and NO, NO_2, and H_2O.

Keywords: Hydroxylammonium Nitrate, Ionic Liquid, Quantum Chemistry

1. Introduction

The United States Air Force desires that future satellites be situationally responsive while maintaining the capability for efficient orbital change and station keeping [1]. One method that can meet these requirements is dual-mode-propulsion which combines the propellant efficiency of electrical propulsion with the high thrust of chemical propulsion into one system. To avoid redundancies, a single propellant is used for both propulsion modes. The current state of the art in-space chemical monopropellant is hydrazine. However, the high volatility and toxicity of hydrazine make it expensive to handle and store [2]. Therefore, replacements for hydrazine have been investigated and developed. One class of propellants is highly energetic molten salts called ionic liquids [3]. Ionic liquids have negligible vapour pressures making them easy to store, and their high molar mass makes them efficient propellants for electric propulsion systems. The ionic liquid of interest in this study is Hydroxylammonium Nitrate (HAN), which has been observed to have beneficial thrust characteristics.

The Aerospace Laboratory for Plasma Experiments (ALPE) at Western Michigan University (WMU) has been investigating the decomposition and ionization of HAN at reduced pressures. The mechanisms for HAN decomposition are extensively discussed in a previous paper (in review). The products of HAN decomposition, as well as the effects of ionized species on the decomposition mechanisms, are discussed in this paper.

2. HAN decomposition

HAN decomposition has been extensively studied in the past. However, the vast majority of research has focused on its decomposition at storage pressures (atmospheric and above). If HAN is to be used in electric propulsion it will be exposed to vacuum conditions. This was shown to significantly change the overall composition of the decomposition products. The relative composition of decomposed HAN at reduced pressures is shown in Table 1.

Table 1. Relative Composition of Decomposed HAN

H_2O	45%
NH_2OH	13%
N_2	12%
H_2	11%
NO_2	6%
NH_3, NO, OH, H_2NO	~2-3% each

Previous studies at elevated pressures observed mostly H_2O, N_2O, N_2 and NO [4,5]. The formation of H_2 and survival of NH_2OH, the neutralized cation of HAN is unique to the vacuum environment and has not previously been measured.

3. Ab-initio Modelling

All quantum chemistry calculations were performed using Gaussian09 software for all calculations [6]. The B3LYP/6-311++g(d) level of theory was chosen for geometry optimizations and for calculating the energetics of transition states. This level of theory has been shown to work well in many situations including the study of ionic liquids [7]. The CBS-QB3 compound method was used to calculate the overall energetics of reactions [8].

To understand the chemistry of partially ionized HAN the potential energy surface of ionized species and ion-neutral pairs was investigated. This was automated through an algorithm performing a constrained randomized search (CRS). The CRS algorithm took a stationary point of an ionized species or ion-neutral pair and randomly mutated the geometry. A transition state search was then performed using Gaussian09's built in Berny algorithm. By reducing or increasing the strength of the mutation the search could be focused to search for a specific reaction or expanded to find more general chemistry. A diagram of this process is shown in Fig. 1.
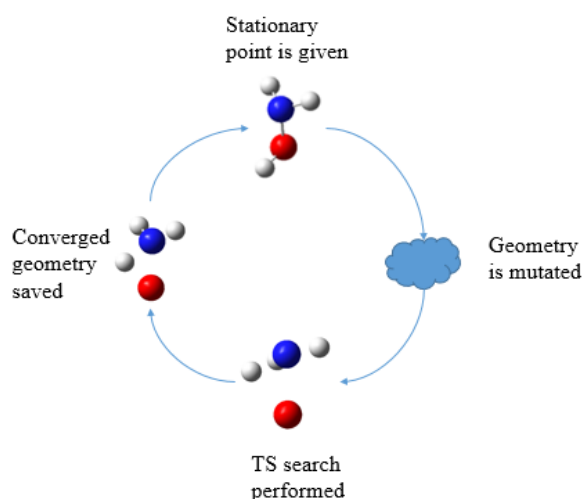
Fig. 1. Diagram of constrained randomized search algorithm used for investigation of HAN potential energy surface.

With this the chemistry of the following species and ion-neutral pairs was investigated.

Table 2. Ion and Ion-neutral pairs investigated

NH_2OH^+	$NH_2OH + N_2^+$
H_2NO^+	$H_2NO + N_2^+$
HNO^+	$HNO + N_2^+$
$NH_2OH + H_2O^+/H_3O^+$	$NH_2OH + H_2^+$
$H_2NO + H_2O^+/H_3O^+$	$H_2NO + H_2^+$
$HNO + H_2O^+/H_3O^+$	$HNO + H_2^+$
$NH_2OH + NH_2OH^+$	$NH_2OH + NO_2^+/NO^+/OH^+$
$H_2NO + NH_2OH^+$	$H_2NO + NO_2^+/NO^+/OH^+$
$HNO + NH_2OH^+$	$HNO + NO_2^+/NO^+/OH^+$

NH_2OH, H_2NO, and HNO were chosen as the neutral species to be investigated not due to their abundance after decomposition, but due to their importance in HAN the overall process of neutral HAN decomposition. Figure 2 shows a diagram of how neutral HAN decomposes.
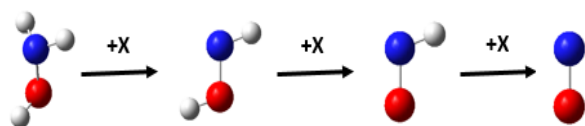

Fig. 2. Primary decomposition pathway of Hydroxylammonium Nitrate. Red, blue and white balls mark oxygen, nitrogen and hydrogen respectively.

This is quite simplified as the process is much more circular with NH_2OH continually being formed and decomposed. However, this still captures the general process where NH_2OH repeatedly loses hydrogen atoms through proton transfer to radicals. With the addition of

new radicals by ionization this cycle could be interrupted and changed. H_2O is by far the most abundant product of HAN decomposition followed by NH_2OH, N_2 and H_2 so the majority of computational time was given to determine reactions with these species as they would most likely make up the majority of the ions in HAN plasma. NO_2, NO and OH were also included as large amounts of these species are produced and consumed during neutral HAN decomposition.

Energetics for the chemistry of reactions involving H_2O^+, NO^+, and NO_2^+ with NH_2OH are shown in Table 3. H_2O^+ was chosen as it is by far the most abundant ion in partially ionized HAN. However, investigations of the HAN potential energy surface (PES) found no reactions with H_2O^+. Instead all reactions preferred H_2O reacting with the NH_2OH^+ ion. These reactions are shown instead. NO and NO_2 are two important radicals in HAN decomposition arising from the decomposition of HNO_3, the anion of HAN, and are included due to their importance in the decomposition of neutral HAN.

Energetics for the reactions were calculated using the CBS-QB3 method and Eqns. 1-11.

$$U_{corr} = E_r + E_v + E_e + E_t \qquad (1)$$

$$H_{corr} = U_{corr} + k_B T \qquad (2)$$

$$S_{tot} = S_r + S_v + S_e + S_t \qquad (3)$$

$$G_{corr} = H_{corr} - TS_{tot} \qquad (4)$$

$$E = E_o + E_{zero} \qquad (5)$$

$$H = E_o + H_{corr} \qquad (6)$$

$$G = E_o + G_{corr} \qquad (7)$$

$$\Delta E = \sum E_P - \sum E_R \qquad (8)$$

$$\Delta H = \sum H_P - \sum H_R \qquad (9)$$

$$\Delta G = \sum G_P - \sum G_R \qquad (10)$$

$$E_a = E_{ts} - E_R \qquad (11)$$

E, U, H and G alone are the zero-point corrected energy, corrected internal energy, corrected enthalpy and corrected free energy, respectively. Subscripts r, v, e and t denote the rotational, vibrational, electronic, and translational contributions. Subscripts R and P denote the reactants and the products. E_o is the electronic energy, E_{zero} is the zero-point energy, E_{ts} is the transition state energy, and E_a is the activation energy.

To obtain the activation energy for each reaction, the intrinsic reaction coordinate was followed from the transition states located using the CRS method. This verified that the TS connected the correct stationary points. This process is shown in Fig. 3.

Table 3. Reaction Energetics for NH_2OH and NO, NO_2, and H_2O

Reaction	E_a (kJ/mol)	ΔE (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
$NH_2OH^+ + H_2O \rightarrow H_4NO_2^+ + H$	459.5	266.4	261.2	352.0
$NH_2OH^+ + H_2O \rightarrow H_3O^+ + H_2NO$	344.8	58.0	58.5	57.1
$NH_2OH^+ + H_2O \rightarrow H_4NO^+ + OH$	303.5	138.1	132.9	222.3
$NH_2OH^+ + H_2O \rightarrow NH_3^+ + H_2O_2$	480.9	160.7	156.7	244.0
$NH_2OH^+ + H_2O \rightarrow NHOH^+ + H_2O + H$	466.0	377.8	273.8	307.0
$NH_2OH^+ + H_2O \rightarrow NHOH_2^+ + H_2O$	215.6	153.1	43.2	152.6
$NH_2OH^+ + NO \rightarrow H_3N_2O_2^+$	292.3	-142.4	-36.8	-47.3
$NH_2OH + NO^+ \rightarrow HN_2O^+ + H_2O$	387.4	-18.1	-12.7	-100.3
$NH_2OH + NO^+ \rightarrow H_2N_2O^+ + OH$	517.1	220.7	224.6	138.3
$NH_2OH + NO^+ \rightarrow HNO^+ + NHOH$	383.6	354.3	235.2	261.7
$NH_2OH + NO^+ \rightarrow NHOH^+ + HON$	551.1	465.3	469.7	376.8
$NH_2OH + NO^+ \rightarrow ONNH_2OH^+$	527.4	-8.4	-12.0	-1.3
$NH_2OH + NO_2^+ \rightarrow H_2NO^+ + HNO_2$	271.7	97.9	103.0	1.6
$NH_2OH + NO_2^+ \rightarrow HONO^+ + H_2NO$	245.5	244.9	251.6	144.7
$NH_2OH + NO_2^+ \rightarrow HNO^+ + H_2N_2O$	331.8	135.0	140.4	40.3
$NH_2OH + NO_2^+ \rightarrow NO^+ + H_3NO_2$	386.8	394.3	398.5	354.3
$NH_2OH + NO_2^+ \rightarrow HONO^+ + NHOH$	315.5	278.3	284.1	178.6
$NH_2OH + NO_2^+ \rightarrow NO^+ + ONH_2OH$	317.2	155.8	160.1	115.4
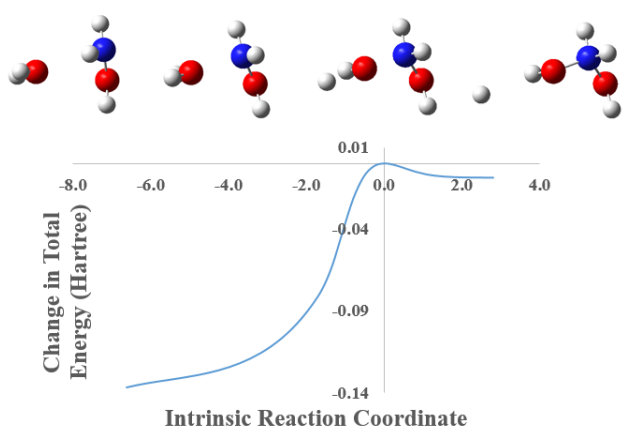
Fig. 3 Intrinsic reaction coordinate of reaction $NH_2OH^+ + H_2O \rightarrow H_4NO_2 + H$. Blue, red and white balls mark nitrogen, oxygen and hydrogen respectively.

The charge density was verified at each stationary point to determine which species was ionized for those cases where the structure did not change after ionization. For NH_2OH this could be ascertained visually as it rotates the OH group by 90° upon ionization as shown in Fig. 4.

The energetics in Table 3 show a great change from the reactions seen for neutral HAN with the same species. With neutral HAN the primary reaction was a proton transfer to radical species. These reactions still exist in ionized HAN, such as the proton transfer to NO to form HNO. However, equally favourable reactions leading to an assortment of radicals and larger species are also observed. The

formation of ONH_2OH is especially interesting as this was believed to be a key intermediate for neutral HAN decomposition to H_2O and HNO. However, reactions to form ONH_2OH are unfavourable in neutral HAN decomposition. This shows one of the many ways ion-neutral reactions will change the chemistry of HAN decomposition.
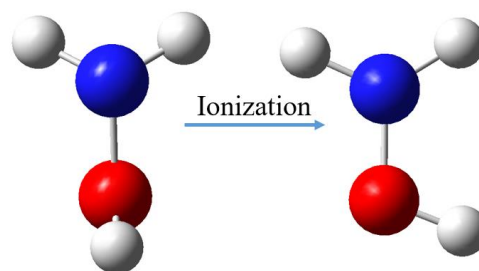

Fig. 4. Change in NH_2OH geometry upon ionization.

4. Conclusions

The plasma chemistry of partially ionized HAN has been investigated through ab-initio modelling. The interactions between key ion-neutral pairs were investigated. Ionization appears to encourage the system to form larger stable species ($H_3N_2O_2^+$, ONH_2OH) through association of ion-neutral pairs. Further, production of radicals (NO, OH, H) is increased through new pathways which were energetically unfavourable in neutral HAN.

5. References

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