

A computational study on the decomposition of NH_4ClO_4 : Comparison of the gas-phase and condensed-phase results

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Abstract

The decomposition of NH_4ClO_4 (AP) in both gaseous and condensed phases has been studied at the CCSD(T)/6-311 + G(3df,2p)//B3LYP/6-311 + G(3df,2p) level. Formation of $\text{NH}_3 + \text{HClO}_3$ is the main channel in the gas phase with 14.2 kcal/mol enthalpy change. In solution, the enthalpy change for this channel is 29.5 kcal/mol, which is close to the sublimation activation energy, ~ 30 kcal/mol in crystalline AP. Formation of $\text{H}_3\text{N}-\text{HO} + \text{ClO}_3$ has higher enthalpy changes, 56.3 kcal/mol and 77.1 kcal/mol in the gas phase and in solution, respectively. Strong solvent effects may exist in the AP decomposition reaction.

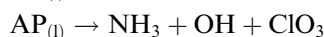
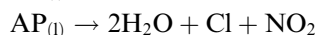
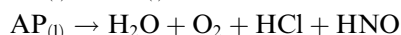
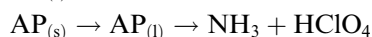
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1. Introduction

Ammonium perchlorate (AP), NH_4ClO_4 , has been widely employed as an oxidizer in composite propellants for rocket propulsion because it is cheap and contains a large amount of oxygen which, in combustion, is converted entirely into stable gaseous reaction products [1–3]. AP is a crystalline material composed of a network of ammonium cations (NH_4^+) and perchlorate anions (ClO_4^-) [4]. Each perchlorate ion is surrounded by seven ammonium ions with the O–N distances ranging from 2.9 to 3.25 Å; similarly, each ammonium ion is surrounded by seven perchlorate ions with H–O hydrogen-bond lengths ranging from 1.891 to 2.077 Å. The ClO_4^- ion has an essentially ideal tetrahedral structure with Cl–O bond length of 1.44 ± 0.01 Å and the bond angle of $109.5 \pm 1^\circ$ [4]; the NH_4^+ ion has a nearly undistorted tetrahedral structure with the average N–H bond length of 1.03 Å.

Despite extensive studies on the mechanism for the decomposition and combustion of AP experimentally over

the past few decades, as summarized in detail in the overviews by Jacobs and Whitehead [3] and Tanaka and Beckstead [5], many questions still remain regarding the key controlling initiation processes within and/or near the burning surface. Tanaka and Beckstead reviewed various assumed initiation reactions; they also put forth a three-phase combustion model (unpublished) to account for the observation of Brill et al. [6] acquired from a time-resolved FTIR measurement at high pressure and that of Ermolin et al. [7] for species detected by mass-spectrometry near a burning AP surface. The mechanism includes the following initiation processes in the solid, liquid and gas phases:



To fully substantiate the three-phase combustion model requires a systematic study of the chemistry occurring in each of the three phases by high-level quantum-chemical calculations for the key processes involved. For the decomposition of AP in solid (crystal), it was believed that the initial step in the low-temperature range ($< 300^\circ\text{C}$) was one of

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the following [8]: proton transfer from the ammonium cation to the perchlorate anion to form ammonia (NH_3) and perchloric acid (HClO_4), electron transfer from the perchlorate anion to the ammonium cation, and Cl–O bond breakage. Proton transfer was believed to be the rate-controlling step with an activation energy of ~ 30.0 kcal/mol [9]. In the past several years, over 60 elementary reactions related to AP decomposition and the formation of its early products from NH_x to ClO_y ($x = 2, 3$; $y = 0-4$) have been investigated in great details in our laboratory, many of which are directly relevant to the chemistry of the Freon-polluted stratosphere. The key results have been reported in a review chapter on propellant chemistry [10].

The decomposition of AP in the gas phase or in solution has not been experimentally or computationally studied. In this work, we have investigated the mechanism for the decomposition of AP in the gas phase and in solution formed by the presence of a small amount of water which may include the moisture in the sample and H_2O formed by redox reactions of NH_3 and HOClO_3 .

2. Computational methods

The geometric parameters of the reactants, products, intermediates and transition states on the potential energy surfaces of the systems studied in this work were optimized at the B3LYP level of theory [11,12] (i.e., Becke's three-parameter nonlocal exchange functional with the non-local correlation functional of Lee, Yang, and Parr [13]) with 6-311+G(3df,2p) basis set. All the stationary points have been identified for local minima and transition states by vibrational analysis. Intrinsic reaction coordinate analyses [14] have been performed to confirm the connection between transition states and designated reactants, products or intermediates. Higher level single-point energy calculations of the stationary points were refined at the CCSD(T)/6-311+G(3df,2p) level, based on the optimized geometries at the B3LYP/6-311+G(3df,2p) level. For the condensed-phase calculations, the polarizable continuum model (PCM) [15,16] as implemented in GAUSSIAN 03 was used to account for the continuum solvation effects. The united atom for Hartree–Fock (UAHF) model was used to build the cavity in PCM, denoted as PCM/UAHF. Water with a dielectric constant of 78 was selected to represent a highly polar condensed-phase medium. All calculations have been carried out using the GAUSSIAN 03 program package [17].

3. Results and discussion

3.1. Decomposition of $\text{NH}_4^+/\text{ClO}_4^-$

3.1.1. Equilibrium geometries and frequencies

The geometries of the intermediates, transition states and products optimized at the B3LYP/6-311+G(3df,2p) are shown in Fig. 1. The values in the parenthesis were obtained by the PCM method in water at the same level.

As shown in Fig. 1, the isolated ClO_4^- and NH_4^+ both have a tetrahedral structure. For ClO_4^- , the Cl–O bond lengths in the gas phase and in solution are 1.457 and 1.455 Å, respectively, which are close to the experimental Cl–O value 1.44 ± 0.01 Å [4] in NH_4ClO_4 crystal; The calculated bond angle, 109.5° is in excellent agreement with the experimental value, $109.5 \pm 1^\circ$ [4]. For an isolated NH_4^+ , the calculated N–H bond lengths are 1.024 and 1.029 Å, respectively, in the gas phase and in solution, which are in good agreement with the experimental values, 1.03 Å [4] and 1.021 ± 0.002 Å [18].

In the gas phase, an ammonium cation and a perchlorate anion cannot co-exist; they may form a meta-stable $\text{NH}_4^+/\text{ClO}_4^-$ complex (LM1) as shown in Figs. 1 and 2. Vibrational analysis shows that all of its frequencies are positive (see Table 1), which indicates that it is a molecular complex. The structure of LM1 shows that the NH_4 and ClO_4 groups in the complex are very distorted from the tetrahedral structure. The ClO1 bond length in LM1 is 0.06 Å longer than that in the isolated ClO_4^- . The hydrogen bond H(1)–O(1), 1.411 Å is much shorter than the experimental value, $1.891 \sim 2.077$ Å [4] in crystal. LM1 can easily convert to the other complex $\text{H}_3\text{N}-\text{HOClO}_3$ (LM2) via a transition state TS1. In LM2, the sharing hydrogen has almost completely transferred from the ammonium group to the perchlorate to form a complex combined by perchloric acid and ammonia. The ClO(1) bond was further increased by 0.138 Å comparing with that in the isolated ClO_4^- . TS1 connects LM1 and LM2, its structure is closer to LM2 (see Fig. 1).

In solution, the complex (LM3) predicted by the PCM method has a looser structure. Two of the four Cl–O bonds are identical with 1.447 Å separation, which is about 0.008 Å shorter than those in the isolated ClO_4^- ion, the ClO1 bond connecting to the NH_4 group increases by around 0.02 Å; the hydrogen bond H(1)–O(1), 1.784 Å, is much closer to the experimental value, $1.891 \sim 2.077$ Å [4] in crystal. Three of the four hydrogens are bound identically to N with the N–H bond length of 1.028 Å which is only 0.001 Å shorter than that in the isolated NH_4^+ , the fourth one is bound more weakly. The $\text{H}_3\text{N}-\text{HOClO}_3$ complex in solution could not be located, no matter what initial structure was given, it was converged directly to give LM3; the result implies that in solution, NH_4^+ and ClO_4^- prefer to be separated, reflecting the effect of solvation as confirmed by the energy diagram discussed in the following section.

There is a structure (TS2) where two hydrogens of the ammonium ion are bonded to two oxygen atoms of the perchlorate to form two identical hydrogen bonds. The bond lengths in the gas phase and solution are 1.672 and 2.078 Å, respectively. Again, the hydrogen bond in solution (2.078 Å) is close to that in crystal ($1.891 \sim 2.077$ Å) [4]. Vibrational analysis indicates that this structure represents the transition state for the ammonium cation 'swinging' between two of the oxygen atoms in ClO_4^- .

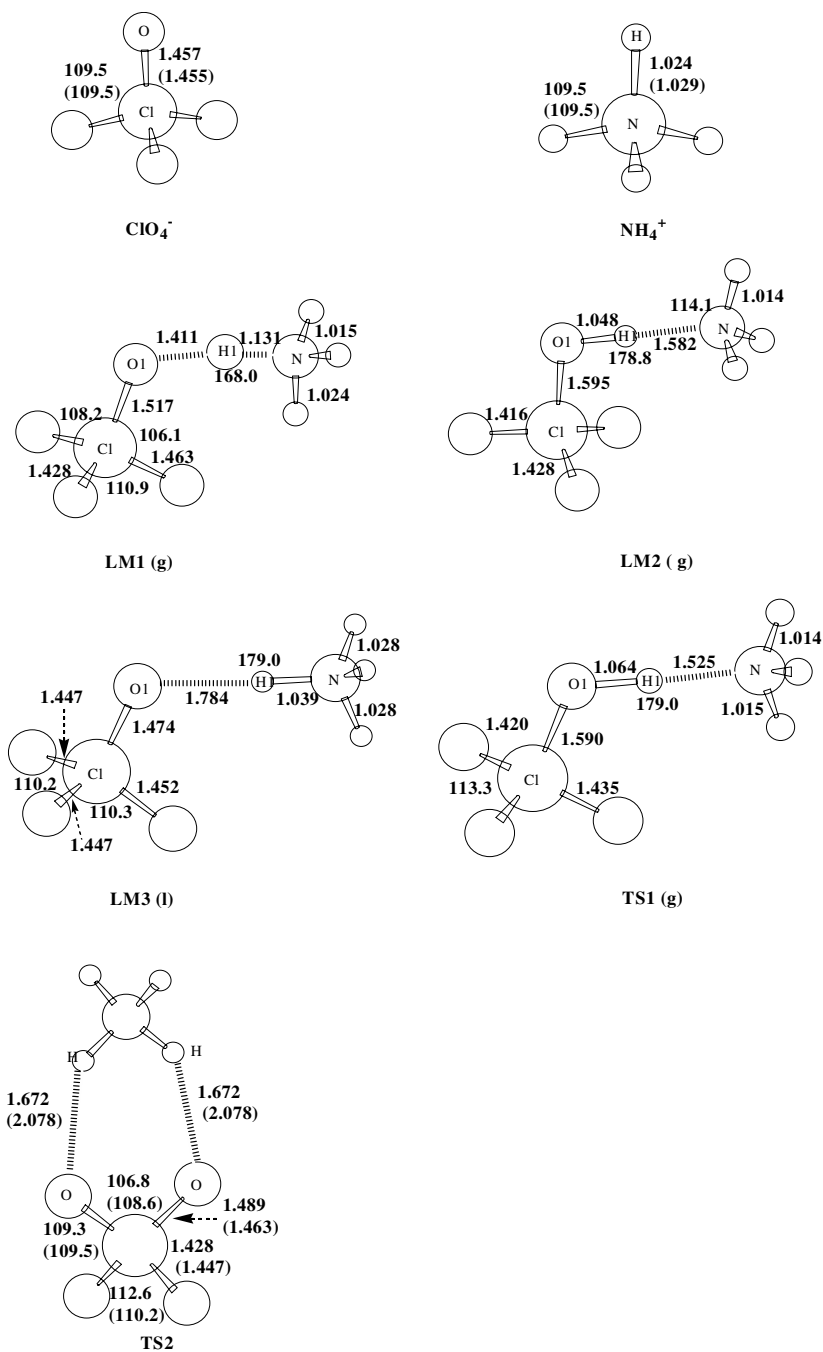


Fig. 1. Optimized geometries for the species involved in the decomposition of NH_4ClO_4 computed at the B3LYP/6-311+G(3df,2p) level. The values in parentheses were obtained for solution by PCM. The bond lengths are given in Å, (angles in degree).

Table 1 shows the calculated frequencies and the available experimental values for NH_3 [19], NH_4^+ [20,21], ClO_3 [22] and HOClO_3 [23]. Comparing the values in Table 1, one can see that the maximum differences between the predicted gas-phase frequencies for NH_3 , NH_4^+ , ClO_3 and HOClO_3 and the experimental values are only 5.3%, 4.0%, 1.7% and 4.6%, respectively. In solution, experimental frequencies for those species listed in Table 1 are not available.

3.1.2. Relative energies

The ZEP-corrected potential energy diagrams obtained at the CCSD(T)/6-311+G(3df,2p)// B3LYP/6-311+G(3df,2p) level for the gaseous and condensed phases are presented in Figs. 2a and b, respectively. As shown in Fig. 2a the activation energy for the transfer of a proton from the ammonium cation to the perchlorate anion in the gas phase at TS1 is only 0.5 kcal/mol, it is considerably lower than the expected value (~ 30.0 kcal/mol) for

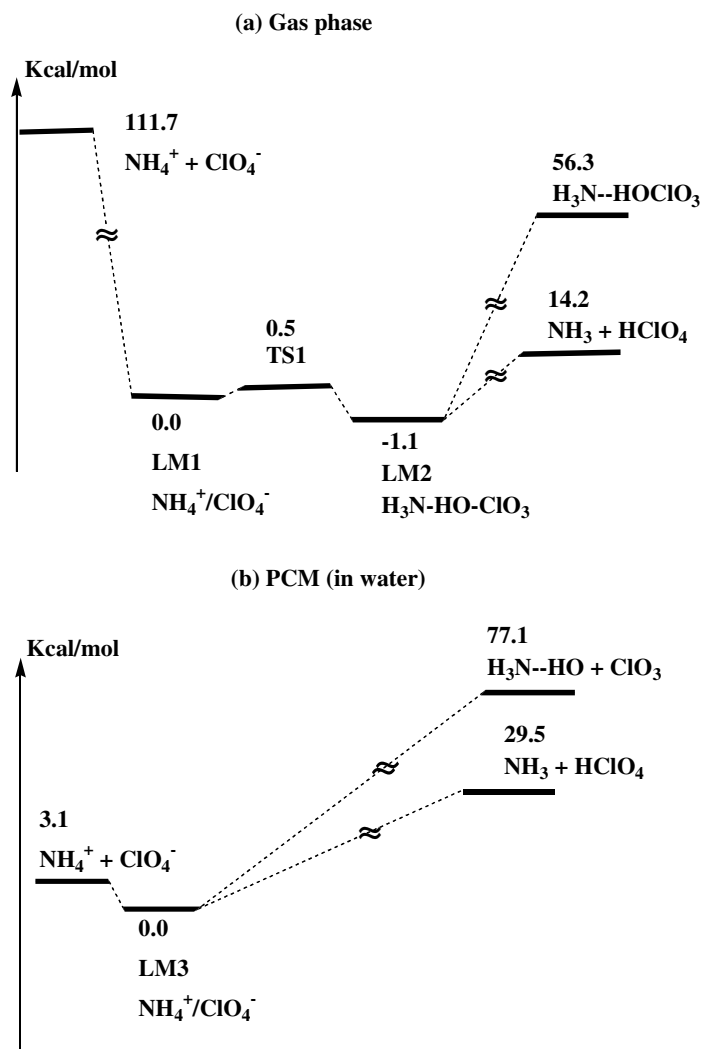


Fig. 2. The schematic diagrams for NH_4ClO_4 dissociation obtained at the CCSD(T)/6-311+G(3df,2p)//B3/6-311+G(3df,2p) level: (a) relative gas phase energies and (b) relative PCM energies in kcal/mol.

the proton transfer process in the crystal [9]. This is expected since the surrounding ionic coulombic attractions and hydrogen-bonding in crystal are not present in the gas phase. As alluded to above, in the crystal the NH_4^+ and ClO_4^- ions are surrounded by each other, they are linked together by the N–H–O type hydrogen bonds, one for each hydrogen, to form a three-dimensional network [4]. To create a neutral molecule by proton transfer, it would likely take a much greater energy penalty for disrupting the ionic matrix. Thus, as expected, the existence of ion pairs in the gas phase is not favored energetically (with 111.7 kcal/mol endothermicity) and the production of perchloric acid and ammonia is preferred with 14.2 kcal/mol endothermicity from the LM1 complex. The second favored channel is the production of ClO_3 and $\text{H}_3\text{N–HO}$ complex with 56.3 kcal/mol heat of reaction.

In solution, the dissociation energy of the $\text{NH}_4^+/\text{ClO}_4^-$ complex (LM3) to $\text{NH}_4^+ + \text{ClO}_4^-$ is only 3.1 kcal/mol, reflecting the effect of solvation as mentioned above. How-

ever, formation of $\text{NH}_3 + \text{HClO}_4$ has to overcome more energy than that in the gas phase by 15.0 kcal/mol; similarly, breaking the Cl–O(1) bond in solution to form $\text{H}_3\text{N–HO} + \text{ClO}_3$ also costs 20 kcal/mol more energy than it does in the gas phase. The result suggests that AP decomposition may be enhanced by a strong solvent effect.

3.1.3. The enthalpies of hydration of NH_4^+ and ClO_4^-

In the preceding section, the predicted structural parameters and frequencies for several species (NH_3 , NH_4^+ , ClO_3 and HOCIO_3) involved in this reaction have been compared with those available experimental values, the agreement is quite satisfactory. To further confirm the reliability of our calculations, the enthalpies of hydration for NH_4^+ and ClO_4^- are compared with available values. For NH_4^+ , the reported data are -76.5 ± 1.4 , -77.9 ± 1.4 and -78.9 ± 4.2 kcal/mol [24] and -82.3 kcal/mol [25]; for ClO_4^- , the reported values are -55.4 ± 1.4 , -54.0 ± 1.4 and -53.1 ± 4.2 kcal/mol [24]. These results are in agreement with the predicted values for NH_4^+ and ClO_4^- ,

Table 1
Vibrational frequencies (cm^{-1}) for the reactants, transition states and products in the gas phase and in aqueous solution, computed at the B3LYP/6-311+G(3df,2p) level of theory^a

Species	Gas	Solution
NH_4^+	1484 (1447), 1723, 3383, 3483 (3343)	1422, 1668, 3274, 3344
ClO_4^-	446, 616, 918, 1093	446, 608, 926, 1065
$\text{NH}_4^+/\text{ClO}_4^-$	33, 114, 136, 330, 385, 427, 438, 506, 599, 622, 642, 813, 956, 1142, 1219, 1263, 1521, 1557, 1645, 1684, 1950, 3405, 3536, 3589,	29, 42, 56, 189, 284, 311, 440, 460, 606, 613, 620, 917, 1022, 1093, 1102, 1412, 1459, 1469, 1692, 1697, 3124, 3308, 3360, 3361
$\text{H}_3\text{N}-\text{HOClO}_3$	22, 45, 79, 252, 359, 399, 426, 469, 583, 586, 589, 769, 1029, 1129, 1172, 1220, 1258, 1565, 1659, 1668, 2351, 3477, 3586, 3593	
NH_3	1029 (974), 1665 (1639), 3479 (3345), 3597 (3447)	1045, 1628, 3408, 3514
$\text{H}_3\text{N}-\text{HO}$	212, 222, 222, 612, 764, 1096, 1630, 1664, 3365, 3476, 3590, 3591	265, 285, 293, 702, 934, 1118 1622, 1638, 2900, 3404, 3505, 3510
HOClO_3	200, 404 (421), 415 (421), 545 (555), 568 (582), 575 (582), 705 (726), 1046 (1048), 1208 (1201), 1256 (1265), 1328 (1326), 3726 (3553)	250, 414, 416, 555, 574, 575, 702, 1035, 1201, 1219, 1295, 3167
ClO_3	472 (476), 472 (476), 564 (566), 921 (905), 1078 (1081), 1078 (1081)	468, 468, 558, 922, 1062, 1062
TS1	35i, 57, 117, 245, 350, 404, 410, 481, 581, 584, 599, 779, 1020, 1159, 1173, 1213, 1254, 1542, 1664, 1664, 2105, 3477, 3588, 3595	
TS2	142i, 19, 241, 283, 319, 373, 430, 499 560, 625, 626, 886, 944, 1123, 1217, 1278, 1491, 1581, 1672, 1686, 2829, 2994, 3523, 3596	254i, 32, 108, 123, 151, 162, 441, 459, 606, 615, 617, 922, 1032, 1073, 1102, 1390, 1432, 1467, 1668, 1681, 3299, 3357, 3391, 3392

The values in parentheses are the experimental gas-phase data.

^a Experimental values for NH_3 [19], NH_4^+ [20,21], ClO_3 [22] and $\text{HO}-\text{ClO}_3$ [23].

–80.1 and –57.2 kcal/mol, respectively, within the uncertainties of the reported values.

4. Conclusions

The activation energy for the transfer of a proton from the ammonium cation to the perchlorate anion to form the $\text{H}_3\text{N}-\text{HOClO}_3$ complex in the gas phase is only 0.5 kcal/mol; it is much lower than the experimentally expected value (~ 30.0 kcal/mol) for the proton transfer mechanism within the crystal. The formation of separated ions in the gas phase is not favored energetically (with 111.7 kcal/mol endothermicity) and the production of perchloric acid and ammonia is preferred with 14.2 kcal/mol endothermicity. On the other hand, in solution the dissociation energy of the $\text{NH}_4^+/\text{ClO}_4^-$ ionic complex to the separated $\text{NH}_4^+ + \text{ClO}_4^-$ is only 3.1 kcal/mol, clearly reflecting the important effect of solvation. However, the formation of $\text{NH}_3 + \text{HO}-\text{ClO}_3$ needs to overcome more energy than that in the gas phase by 15.0 kcal/mol; similarly the formation of $\text{H}_3\text{N}-\text{HO} + \text{ClO}_3$ also costs more energy (20 kcal/mol) than that does in the gas phase. The result suggests a possible strong solvent effect on the AP dissociation kinetics in solution.

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