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Research paper

A vacuum ultraviolet photoionization study on the thermal decomposition of ammonium perchlorate

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ABSTRACT

Pyrolysis products of ammonium perchlorate (NH_4ClO_4) at 483 K were monitored on line and *in situ* via single photon photoionization reflectron time-of-flight spectrometry (PI-ReTOF-MS) in the photon energy range of 9.00–17.50 eV. The photoionization efficiency curves (PIE) of the subliming product molecules were collected and allowed for detection of three class of products containing chlorine, nitrogen, and oxygen including atoms and free radicals. These results suggest a new insight into possible low-temperature decomposition pathways of NH_4ClO_4.

1. Introduction

The degradation of ammonium perchlorate (NH_4ClO_4)—widely exploited as a solid rocket propellant—has been extensively studied both experimentally and computationally for half a century. Yet, the exact decomposition mechanisms and distinction between *primary* and *higher-order products* have remained elusive to date [1]. Previous investigations suggest that NH_4ClO_4 has two distinct decomposition pathways at "low" (below 510 K) and "high" temperatures (above 620 K). The first step in the thermal decomposition has been proposed to be initiated by a proton transfer from the ammonium moiety (NH_4^+) to the perchlorate anion (ClO_4^-) resulting in the formation of ammonia (NH_3) and perchloric acid ($HClO_4$, (R1)). These primary decomposition products can take part in multiple consecutive reactions [1–6].

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4 \quad (R1)$$

Bircumshaw and Newman pioneered the experimental investigations examining the thermolysis of NH_4ClO_4 *in vacuo* in the temperature ranges of 493–553 and 653–723 K (Table 1) [7]. The authors concluded that at low temperatures, only 30% of the reactant decays; the solid residue was found to be porous suggesting that the decomposition takes place throughout the material. Furthermore, a phase transition of NH_4ClO_4 from orthorhombic to cubic was observed at 513 K. Finally, this work detected multiple gaseous decomposition products at low temperatures: molecular chlorine (Cl_2), nitrous oxide (N_2O), dinitrogen tetroxide (N_2O_4), molecular oxygen (O_2), nitrogen (N_2), water (H_2O), hydrogen chloride (HCl), chlorine dioxide (ClO_2), and $HClO_4$.

The first mass spectrometric (MS) detection of the decomposition products was performed by Heath and Majer [8]. This study revealed that the decomposition takes place in the solid phase with the predominant fragmentation leading to gas-phase NH_3 and $HClO_4$; this finding was corroborated by Inami et al. [2]. A subsequent MS study concluded that the thermal decomposition of NH_4ClO_4 yielded principally H_2O, N_2O, Cl_2, and O_2 along with HCl and N_2 [9]. Gas chromatography (GC) was also applied to detect the thermolysis products as O_2, N_2, N_2O, Cl_2, ClO_2, nitric acid (HNO_3), HCl, and nitric oxide (NO) [10]. This study proposed that the low-temperature decay represents an autocatalytic process starting with the decomposition of NH_4ClO_4 to adsorbed NH_3 and $HClO_4$. This first step is then followed by the autoprotonation transforming the primary product $HClO_4$ into H_2O plus the chlorine trioxide cation (ClO_3^+); the latter was speculated to oxidize NH_3 to higher order products such as nitrogen oxides as observed. Scanning electron microscopy (SEM) and optical microscopy were also employed to monitor the degradation of NH_4ClO_4 [11,12].

Later, an attenuated total reflection (ATR) infrared study confirmed the phase transition at 523 K; however, this study could not detect any new species formed in the solid or in gas phase [13]. The time-of-flight (TOF) mass spectrometry (MS) coupled with electron impact (EI) ionization was first utilized by Boldyrev et al. detecting not only the primary decomposition products NH_3 and $HClO_4$, but also chlorine trioxide (ClO_3), ClO_2, chlorine monoxide (ClO), chlorine atoms (Cl), and amidogen (NH_2) [14]. Hackman et al. exploited TOF-MS and observed the nitrosyl

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Table 1
Previous experimental results on the low-temperature decomposition of NH_4ClO_4.

p (mbar)	T (K)	Detection	Products	Reference
'vacuum'	493–553	Chemical analysis	$HClO_4$, ClO_2, Cl_2, HCl, H_2O, N_2, O_2, N_2O, N_2O_4	7
'very low pressure conditions'	393–473	MS	Various fragments of NH_4ClO_4 and $HClO_4$	8
10^{-3}	503	MS	H_2O, N_2O, Cl_2, O_2, HCl, N_2	9
'in He flow'	523–598	GC, Chemical Analysis	O_2, N_2, N_2O, Cl_2, ClO_2, HNO_3, HCl, NO	10
27	499	SEM	–	11
7×10^{-2}, 1000	484–504	OM	–	12
N/A	523	ATR IR	No products could be identified	13
N/A	523–773	TOF-MS	NH_3, $HClO_4$, ClO_3, ClO_2, ClO, Cl, NH_2	14
10^{-5}	368–438	TOF-MS	$HClO_4$, ClO_3, ClO_2, ClO, HCl, Cl, O_2, HNO, NO, NH_4, NH_3, OH, NH_2, NH	15
'in N_2 flow'	300–625	Raman spectroscopy	No products were identified	16
N/A	460–510	Gas analysis, SEM	NO_2ClO_4 intermediate, NO^+, ClO_3^-, 2O, O_2, N_2	17
'in N_2 flow'	488–658	DSC, HPLC, GC	O_2, Cl^-, N_2O, ClO_3^-, N_2, Cl_2, NH_4^+	18
N/A	293–623	DSC, TGA, SEM, QMS	N_2O, NO	19, 20
'in Ar flow'	303–773	TGA/DSC–FT-IR/MS	N_2O, NO_2	21
'low pressures'	303–773	TGA–FT-IR/MS	FT-IR: N_2O, HCl, NO_2, HNO_3 QMS: H_2O, Cl_2, O_2	22
'low pressures'	303–773	TGA–FT-IR/MS	FT-IR: NH_3, N_2O, HCl, NO_2, H_2O, NO, HNO_3 QMS: Cl_2, O_2, HOCl, ClO, NH_4Cl	23

hydride (HNO) for the first time [15]. Besides, hydrides of nitrogen other than NH_3 such as the ammonium radical (NH_4), NH_2, and imidogen (NH) might also play a role in the decomposition mechanisms according to their findings. $HClO_4$, Cl, and simple chlorine oxides like ClO, ClO_2, and ClO_3 radicals were detected, too. However, they found no evidence for the presence of Cl_2, hypochlorous acid (HOCl), chlorous acid ($HClO_2$), chloric acid ($HClO_3$), chlorine tetroxide (ClO_4), N_2, N_2O, and nitrogen dioxide (NO_2). Here, the authors proposed the decay of $HClO_4$ into ClO_3 and hydroxyl radicals (OH) as opposed to an autoprotonation process. Subsequently, Brill and Goetz utilized Raman spectroscopy to monitor the phase change in NH_4ClO_4 between 300 and 625 K [16]. Galwey and Mohamed speculated on nitryl perchlorate (NO_2ClO_4) as a reaction intermediate based on its high thermal instability and the observation of oxidized nitrogenous species like nitrogen monoxide cation (NO^+) [17].

The use of differential scanning calorimetry (DSC), high-performance liquid chromatography (HPLC), and gas chromatography (GC) revealed the presence of O_2, N_2, Cl_2, chloride (Cl^-) and chlorate (ClO_3^-) anions, N_2O, and NH_4^+ [18]. Low-temperature decomposition of NH_4ClO_4 and its partly and/or completely deuterated isotopologue ($NH_{4-x}D_xClO_4$) was examined by Majda et al. via DSC, SEM, thermogravimetric analysis (TGA), and quadrupole MS (QMS) techniques [19,20]. These studies showed that the decay rate depends on the degree of deuteration; furthermore, the volume fraction of the pores of the deuterated sample appears to be lower compared to the non-labeled counterpart. The authors concluded that the effects can be best rationalized as caused by a proton transfer at the intersections of dislocations in the bulk of the crystals. It is worth noting that N_2O and NO were detected via MS as primary decomposition products of the low-temperature and high-temperature decompositions, respectively.

Thereafter, a TGA/DSC–MS/FT-IR analysis showed that the formation of N_2O and NO_2 is strongly temperature dependent [21]. Three distinct decomposition stages were proposed: an autocatalytic pathway, a low-temperature diffusion, and a high-temperature stable-phase reaction. The degradation occurs inside the pores of the sample beneath the surface, where the primary products NH_3 and $HClO_4$ are adsorbed. The latter adsorbs more rapidly, thus the concentration of NH_3 in the gas phase was found to be higher. As $HClO_4$ decomposes into other chlorine oxides like ClO_2, these oxides were suggested to facilitate the gas-phase oxidation of NH_3 [1]. At high temperatures, the products formed inside the sample can take part in higher order subsequent reactions both at the surface and in the gas phase. Recent TGA–FT-IR/EI-MS studies detected N_2O as the primary product of the low-temperature degradation of NH_4ClO_4 followed by HCl, NO_2, and HNO_3 [22,23]. H_2O, Cl_2, and O_2 were observed via the electron ionization mass spectrometry. Interestingly, NO could not be identified. The effect of grain size was also probed [23]. Kinetic studies and the effect of pressure on the degradation mechanisms were investigated exploiting TGA and DSC methods and are summarized in Table S1 in the Supplementary Material.

Extensive theoretical studies have also been conducted as they were summarized in our previous work on NH_4ClO_4 decomposition [24]. The computational efforts by Lin et al. proposed the mechanism and determined rate constants of reactions that occur during the thermolysis of NH_4ClO_4 [25,26]. The calculations agree with the experimental results and consider (R1) as the first reaction that takes place during the pyrolysis, followed by the unimolecular decomposition of $HClO_4$ into ClO_3 and OH [27]:

$$HClO_4 \rightarrow ClO_3 + OH \quad (R2)$$

which is succeeded by the reaction of the product molecules into ClO_2 and hydroperoxyl radical (HO_2) [27]:

$$ClO_3 + OH \rightarrow ClO_2 + HO_2 \quad (R3)$$

The unimolecular decomposition of the chlorine oxides by atomic oxygen loss might also be an important pathway [28,29]. The oxygen atoms (O) [30] and chlorine oxides [31] may for instance take part in the oxidation of NH_3, therefore accounting for the formation of various nitrogen oxides. The reaction of oxidants with the NH_3 decomposition product NH_2 was also investigated by theoretical methods [32,33].

However, despite extensive investigations, no coherent picture has emerged to date on the reaction pathways and products during the thermolysis of NH_4ClO_4 within a single experimental setup. Strong discrepancies between the experimental and theoretical results are evident [1,25,34]. The current work aims to present a comprehensive, unbiased picture on *all products* that may be important during the thermolysis of NH_4ClO_4 by *exploiting a single, versatile experimental technique*. This is done by detecting *all* degradation products for the first time under controlled conditions on line and *in situ* via state-of-the-art single vacuum ultraviolet (VUV) photoionization coupled with reflectron time-of-flight mass spectrometry (PI-ReTOF-MS). Compared to traditional mass spectrometry utilizing EI or off line GC–MS and HPLC analysis, this technique has unique advantages. The EI results not only in the ionization of the parent molecule, but also in its extensive fragmentation; this may make the structural identification, e.g. that of the isomers, difficult. These can be easily avoided by using the PI-ReTOF-MS method since the photon energy can be chosen thus the fragmentation does not take place [35]. Moreover, the structural isomers can also easily be separated based on their distinct