

A reaction network of AP decomposition: the missing piece from atomic simulations

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Abstract

The decomposition network of AP is essential for the combustion performance and safety of solid propellants, while the detailed reaction pathway during thermolysis is far from clear due to the ultrafast and complex reactions involved. Herein, we present direct atomic simulations of AP thermal decomposition and propose a detailed decomposition network to fill the missing piece in the kinetics models, by using a neural network model derived from *ab initio* calculations. The proton transfer is the dominant channel ($\text{NH}_4 + \text{ClO}_4 \rightarrow \text{NH}_3 + \text{HClO}_4$), which is also observed in previous mass spectra experiments. In addition, gas products from decomposition play a critical role in promoting the decomposition of solid AP. For example, the H abstraction reaction by OH is found to be a critical pathway for AP decomposition. These simulations provide atomic insights into the complex reaction dynamics of AP and can be extended to investigate the reaction mechanism of novel energetic materials.

Keywords: Ammonium perchlorate; Decomposition; Reaction mechanism; Neural network potential; Molecular dynamics

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1. Introduction

The solid propellant is used in a wide range of rocket applications, including defense missiles and booster rockets for space applications. Ammonium perchlorate (AP), as one of the most important oxidizers, has been widely applied to many advanced solid propellant formulations, such as AP/HTPB, AP/HTPB/Al/HMX [1] and AP/GAP/Al/Cl-20 [2]. Thermal decomposition is a fundamental process for any energetic material (EM) exposed to external stimuli. It relates to the ignition of explosives, the subsequent detonation performance, and their sensitivity from mechanical stimuli to direct heating [3]. Therefore, a comprehensive understanding of thermal decomposition is essential for the combustion performance and safety of AP-based propellants.

AP decomposition has been investigated in abundance by extensive experimental works, including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and mass spectrometry (MS). AP decomposition is a complex process that includes an endothermic phase transition and exothermic reactions, and these processes are strongly affected by the environmental conditions and sample properties [4,5]. Using a mass spectrometer, NH_3 , HCl , Cl_2 , O_2 , and small amounts of nitrogen oxides were identified by Heath and Majer [6] in the products. A later work [7] supports the same findings using time-of-flight velocity spectra (TOFVS), which are able to accurately capture the intermediates before they undergo secondary reactions in a mass spectrometer. They further identified HClO_4 , ClO_3 , ClO_2 , ClO , Cl , and NH_2 as the intermediates during AP decomposition. Despite previous efforts to understand the kinetics and products of AP decomposition, the reaction mechanism during thermolysis is missing due to the ultrafast and complex reactions involved, which can hardly be captured in experiments [8]. Nevertheless, most previous works have focused on gas-phase reactions, while solid- and liquid-phase processes remain obscure. Therefore, most AP simulations rely on simple models to describe thermal decomposition with limited empirical data for validation [9,10]. A detailed decomposition mechanism remains as the missing piece in AP combustion models. Recently, additives such as fuel metals [11,12], energetic materials [13,14], and catalysts [15] have been added to propellants to improve their combustion characteristics. Although the simple models could describe the kinetics of AP monopropellants, they can hardly handle the chemical coupling between AP and additives. Overall, a detailed decomposition mechanism is required for the combustion simulation of AP-based propellants.

In the past two decades, the reactive molecular dynamics (MD) method has been a popular tool to investigate complex physical and chemical behaviors at the atomic scale. It has been applied to reveal the decomposition mechanism of energetic materials, such as RDX and CL-20 [16,17]. Unfortunately, no proper potential model for AP decomposition exists to date. Herein, the development of a reactive potential is urgent for understanding AP decomposition. In this communication, a reactive potential of AP is developed based on *ab initio* calculations for the first time. Direct atomic simulations of AP thermal decomposition are carried out to extract the kinetic evolution of AP decomposition. A reaction network is proposed to fill the missing piece in the AP model.

2. Computational methods

The potential energy surface (PES) is represented by a deep neural network using the Deep Potential (DP) scheme [18]. In Fig. 1, the training dataset consists of trajectories from *ab initio* MD simulations. Then, a neural network potential (NNP) model is developed that interprets the atomic coordination (R) into interatomic forces (F) and energies (E), which enable MD simulations at a large spatial and time scale with an *ab initio* level of accuracy. The deep neural network contains a filter (embedding) network with three layers (25, 50, and 100 nodes/layer) and a fitting net with three layers (240 nodes/layer). Similar to a classical neural network, the DP scheme trains the model by computing the gradient of the loss function using the back-propagation algorithm. The NNP is trained for 4.0×10^6 iterations with an exponentially decaying learning rate from 1.0×10^{-3} to 5.0×10^{-8} . The unit cell of the orthorhombic AP crystal is used to prepare the training sets. A set of reactive MD simulations are performed for 1 ps to obtain trajectories under an NVT ensemble at temperatures of 300, 1000, 2000, 3000, and 4000 K. Since the reactive potential for AP decomposition does not exist, *ab initio* MD simulations are directly calculated using CP2K [19]. Core electrons are treated using Goedecker–Teter–Hutter (GTH) pseudopotentials and the Perdew Burke Ernzerhof (PBE) generalized gradient approximation method. A double-zeta Gaussian basis set plus polarization (DZVP-MOLOPT) is considered. Other detailed settings are included in previous works on NNP development [20,21]. To evaluate the model accuracy, the potential energies and forces (Fig. S1), lattice constant (Table S1), equation of state (Fig. S2), and reaction enthalpies (Table S2) are calculated with the NNP. Predictions for all properties show good agreement with *ab initio* calculations.

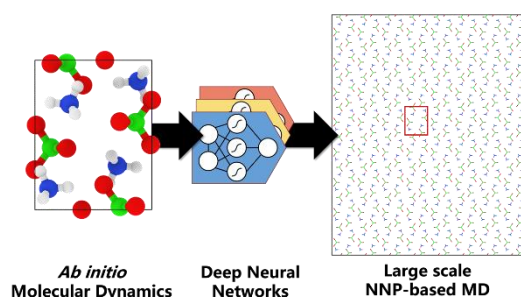


Fig. 1 Illustration of the training process.

To obtain the detailed decomposition mechanism of AP, MD simulations are performed on a $4 \times 4 \times 4$ supercell using our NNP model. The system was initially equilibrated at 300 K with an isothermal–isochoric (NVT) ensemble for 10 ps to equilibrate the structure. Then, the system was linearly heated toward 3000 K at a rate of 30 K/ps. The equations of motion are integrated by the velocity Verlet method with a time step of 0.1 fs. A Nose–Hoover thermostat is applied with a dump parameter of 20 fs implemented on the LAMMPS package [22]. ReacNetGenerator [23] is used to extract species and reactions from the MD trajectories.

3. Results and discussion

MD simulation is performed using the NNP model to investigate the thermodynamic properties of AP when heating from 300 to 3000 K. This setup is selected to simulate the thermal heating stimuli of TGA/DSC experiments. The time evolution of the mass fraction of AP and heat flow rate are provided in Fig. 2. At ~ 60 ps,

there is an endothermic peak in the heat flow corresponding to the phase transition of AP. It is immediately accompanied by an exothermic peak (~ 70 ps) due to thermal decomposition. At ~ 80 ps, the mass fraction of AP approaches 0. Further heating of the system leads to another exothermic peak at ~ 85 ps. The above results agree with the trends in previous TGA/DSC experiments [4,5]. The endothermic peak is usually assumed to be a morphological transition from an orthorhombic to a cubic phase. In Fig. S3, we examined the morphology and atomic trajectories of AP at 50 and 60 ps. It is found that the AP molecules at the endothermic peak ($t=60$ ps) behave as an amorphous phase rather than a cubic phase, where both NH_4 and ClO_4 groups overcome the constraints of their lattices and turn into random thermal motions.

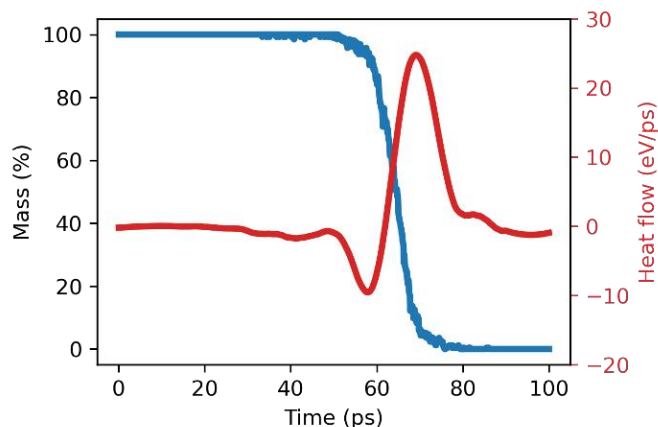


Fig. 2 Mass fraction of AP (left axis) and simulated heat flow (right axis) at a heating rate of 30 K/ps.

Figure 3 exhibits the time evolution of intermediates and products in the AP decomposition process. In total, 36,330 kinds of species are observed in the simulation, and the major species are plotted in Fig. 3a according to their maximum concentrations. Specific focus is given to minor intermediates in the range of 40-80 ps (Fig. 3b). At ~ 50 ps, the observation of NH_3 , HClO_4 , and ClO_3 indicates H transfer from NH_4 to ClO_4 , forming HClO_4 and NH_3 , which is consistent with the well-established proton transfer mechanism in AP decomposition [24]. The final products, including H_2O , O_2 , NO , Cl_2 , HCl , and N_2 , are formed at approximately 70 ps, and these species reach equilibrium after 90 ps. The production of final products accounts for the exothermal peak at approximately 70 ps. The production of HCl , Cl_2 , N_2 , and NO is observed in mass spectrometry experiments [7,25].

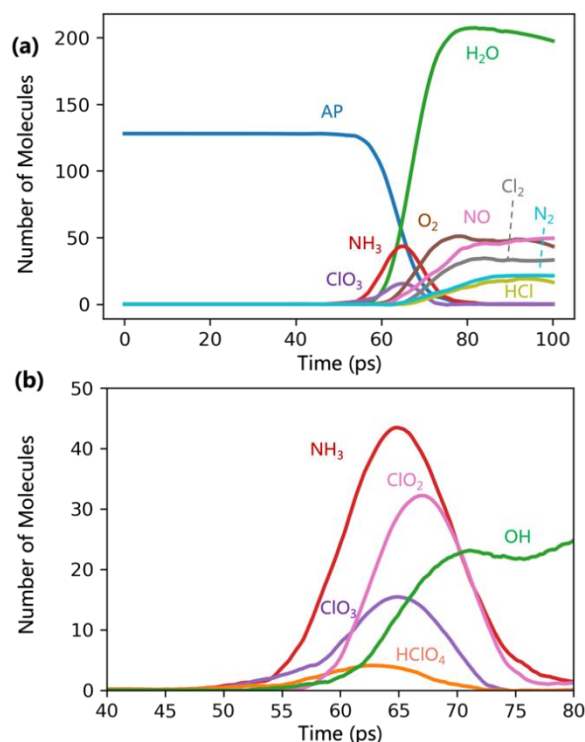


Fig. 3 (a) Major and (b) minor gas-phase species during AP decomposition predicted by the NNP model.

Figure 4 shows a reaction network of AP decomposition, where the elementary reactions are extracted from atomic trajectories. As suggested by Bernigaud et al. [26], the overall decomposition kinetics can be divided into four groups: the primary decomposition of AP, hydrogen chemistry, nitrogen chemistry and chlorine chemistry. All the elementary reactions of AP decomposition are included in Table S3 (see supplementary materials). The reaction network is compared with previous AP mechanisms [26,27], and pathways revealed by the MD trajectories are represented with dashed lines to fill the missing piece (Fig. 4). In the first group of primary decompositions, the decomposition reaction is mostly initialized by a proton (H) transfer reaction from the NH_4 cation to the ClO_4 anion. This causes the formation of an important compound, e.g., HClO_4 . In addition, direct decomposition of NH_4 and ClO_4 is also observed to produce H and O radicals. The frequencies of the above reactions are extracted from MD trajectories as 192, 43, and 17. It is demonstrated that the proton transfer reaction is the primary reaction for AP decomposition at the first stage. This reaction, i.e., $\text{NH}_4 + \text{ClO}_4 \rightarrow \text{NH}_3 + \text{HClO}_4$, is treated as the primary decomposition pathway in many AP combustion models [9,10]. However, this is the first study to observe the hydrogen abstraction reaction as an important pathway. A similar hydrogen abstraction reaction is commonly seen in other reactive materials, such as hydrocarbons and RDX [28], but it is not reported in AP decomposition.

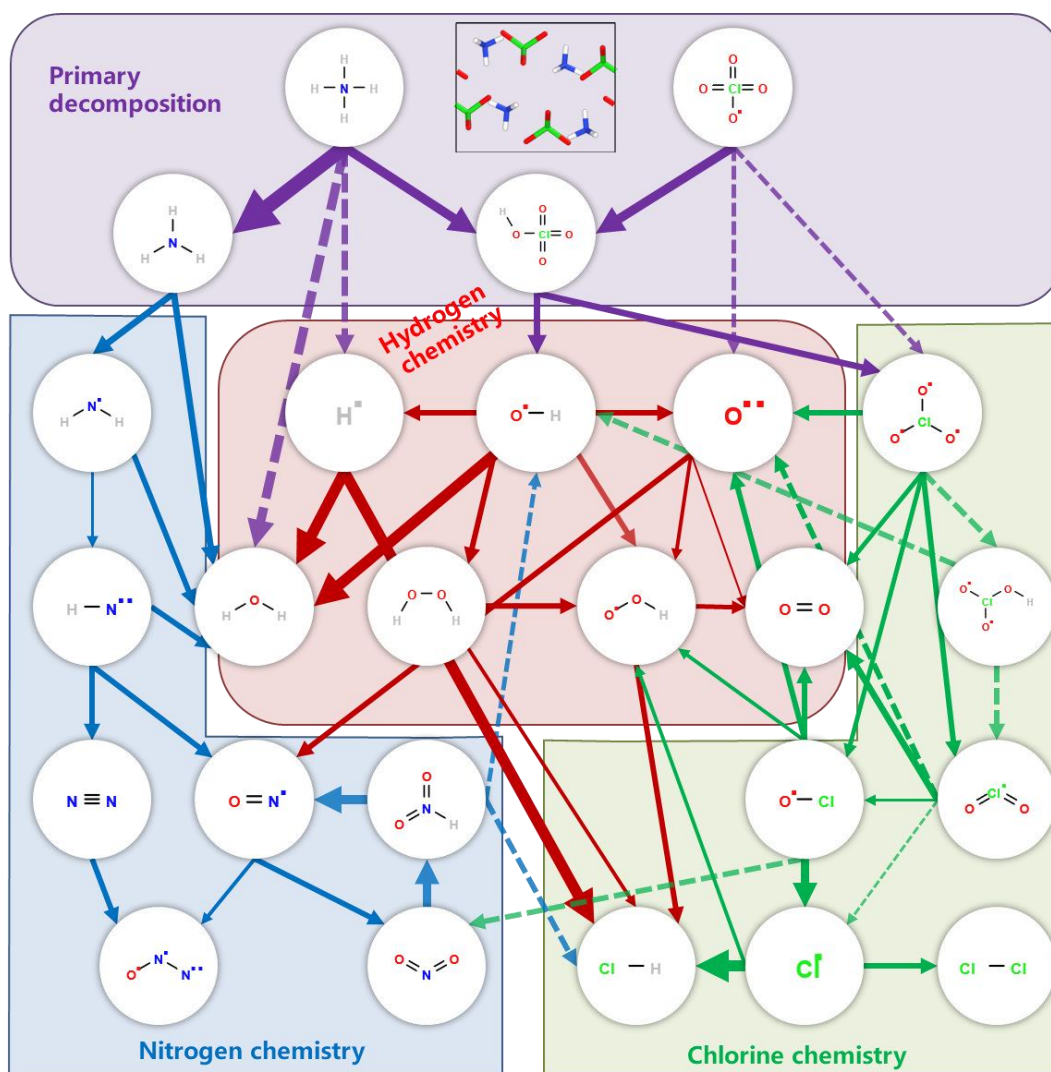


Fig. 4 Primary reaction pathways in AP decomposition. The arrow width represents the observed number of reactions (n), where width = $\ln(n+1)$. The overall kinetics include four groups, e.g., primary decomposition of AP, hydrogen chemistry, nitrogen chemistry and chlorine chemistry. The dashed lines represent the pathways revealed by the MD simulations for the first time.

The HClO₄ molecules are very reactive and quickly decompose, where the O-Cl bond length gradually increases and finally forms OH and ClO₃. As a result, the amount of HClO₄ remains at a low value in Fig. 6b. Particular attention should be paid for the pathway via hydrogen abstraction by OH to convert NH₄ into NH₃. This pathway is comparable to $\text{NH}_4 + \text{ClO}_4 \rightarrow \text{HClO}_4 + \text{NH}_3$ but is not considered in previous mechanisms [26,27]. A recent MS experiment [29] also supports our findings, where the gas products play a role in promoting/retarding the decomposition of solid AP. In the detailed reaction network for AP decomposition, we also discovered several other bimolecular reactions that have not been experimentally reported, for example, $\text{NH}_4 + \text{NH}_2 \rightarrow 2 \text{NH}_3$ and $\text{ClO}_4 + \text{NH}_3 \rightarrow \text{HClO}_4 + \text{NH}_2$. These bimolecular reactions between gas species and AP could affect the AP decomposition process and should not be ignored in the development of the detailed mechanism.

After primary decomposition, nitrogen chemistry, hydrogen chemistry, and chlorine chemistry reactions proceed simultaneously. Nitrogen and hydrogen chemistry has been well established in previous works [26,27]. However, studies on chlorine chemistry are inadequate. A new intermediate, e.g., HClO₃, is reported. It is an important product of ClO₃ through $\text{ClO}_3 + \text{NH}_4 \rightarrow \text{HClO}_3 + \text{NH}_3$. This pathway is preferable to the ClO₃

decomposition pathway ($\text{ClO}_3 \rightarrow \text{O}_2 + \text{ClO}$). In addition, several new pathways related to HClO_3 have also been reported, such as $\text{HClO}_3 \rightarrow \text{ClO}_2 + \text{OH}$ and $\text{OH} + \text{HClO}_3 \rightarrow \text{ClO}_3 + \text{H}_2\text{O}$.

4. Conclusions

A detailed reaction network for AP decomposition is proposed from atomic simulations using a neural network potential, which fills the missing piece for AP combustion. As the temperature rises, AP molecules experience an endothermic peak for phase transition and an exothermic peak for thermal decomposition. Proton transfer and OH abstraction are found to be the most favorable routes of decomposition. This work illustrates the power of atomic simulation to provide insights into the detailed mechanism of decomposition from the *ab initio* level of theory and opens new opportunities to build reaction kinetics models for complex reactive systems. Moving forward, a more detailed understanding of the decomposition mechanism of other propellant components, such as HTPB, energetic materials and metal catalysis, is needed in future works.

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