



## Low-temperature thermal decomposition of crystalline partly and completely deuterated ammonium perchlorate

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### ABSTRACT

Although ammonium perchlorate, widely used as a rocket propellant, has been extensively investigated for many years, the mechanism of its thermal decomposition at low temperatures remains controversial. Examination of the thermal behaviour of large crystals of partly and completely deuterated ammonium perchlorate by DSC, SEM, TG and QMS reveals that the rates of thermal decomposition depend on the degree of deuteration and decrease in the sequence  $N[H/D]_4ClO_4 > NH_4ClO_4 > ND_4ClO_4$ .

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### 1. Introduction

Although various aspects of the chemistry of ammonium perchlorate have been examined, some questions remain unanswered and the compound is being actively studied. Most recent publications attempt to tailor the thermal behaviour of ammonium perchlorate, both pure and within composite propellants, using very diverse catalysts such as nitrogen-doped ZnO nanocrystallites with a one-dimensional structure [1]; 3D (6,8)-connected metal-organic framework  $\{[Cu_5(trz)_2(mal)_2(fma)(H_2O)_4]2H_2O\}_n$  [2]; NdCrO<sub>3</sub> nanoparticles [3]; lead (II) *N,N*-bis[1(2) H-tetrazol-5-yl] amine compounds [4]; core-shell-structured Co<sub>3</sub>O<sub>4</sub> microspheres [5]; carbon nanotube-neodymium oxide composite [6] and self-assembled CuO nanoarchitectures [7]. The structures of the various solids involved are very different [8] and that finding a successful catalyst requires a combination of chemical intuition, diligence and fortune. Despite much effort to understand the mechanism of thermal decomposition of ammonium perchlorate (for review see [9,10]) controversial issues remain such as the nature of the 'low-temperature' thermal decomposition which occurs below ca. 240 °C, the temperature of phase transition from the orthorhombic to the cubic phase. Decomposition stops at ca. 30% conversion to a porous ammonium perchlorate, the effect known since 1955 [11], but never satisfactorily explained. Many experimental and theoret-

ical results (reviewed in [9]) support the hypothesis that thermal decomposition proceeds via proton transfer likely to occur at the intersections of dislocations in the bulk crystals [12]. However, *ab initio* molecular dynamics simulations [13,14] conclude that there should be no proton transfer in a perfect crystal lattice of ammonium perchlorate. A recent DFT study [15] favours sublimation of H<sub>3</sub>N-HOClO<sub>3</sub> acid-base molecular complex with subsequent proton transfer in the gas phase. While these results are certainly relevant to high-temperature thermal decomposition, they cannot explain why low-temperature decomposition begins inside the crystals and not on their surfaces.

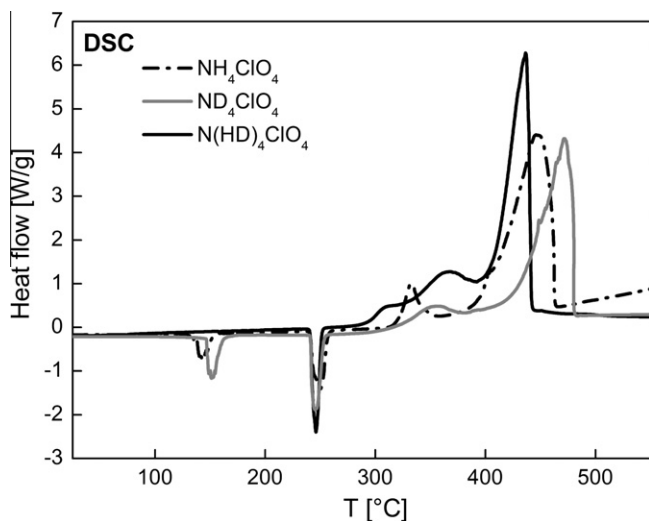
To resolve these interrelated questions we compared the thermal behaviour of large crystals of NH<sub>4</sub>ClO<sub>4</sub> and ND<sub>4</sub>ClO<sub>4</sub> [12] and found that the rate of thermal decomposition of deuterated samples is lower. Since additional insights into the mechanism of decomposition may be gained by examining thermal properties of partly deuterated samples, we have used SEM, DSC, TG and QMS to examine single crystals of ND<sub>4</sub>ClO<sub>4</sub>, N[H/D]<sub>4</sub>ClO<sub>4</sub> and NH<sub>4</sub>ClO<sub>4</sub>. In DSC and TG experiments we compare the thermal behaviour of bulk and plate crystals.

### 2. Methods

Parent single crystals were prepared as follows. N[H/D]<sub>4</sub>ClO<sub>4</sub>: 4.86 g of 70 wt.% solution of HClO<sub>4</sub> in H<sub>2</sub>O was added to 20 g of H<sub>2</sub>O; then 5.2 g of 25 wt.% NH<sub>4</sub>OH was added dropwise. A tightly closed flask with the mixture was placed in a refrigerator for 3 days. The crystalline product NH<sub>4</sub>ClO<sub>4</sub> (1.124 g) was filtered off and recrystallised three times from the solution of H<sub>2</sub>O:D<sub>2</sub>O

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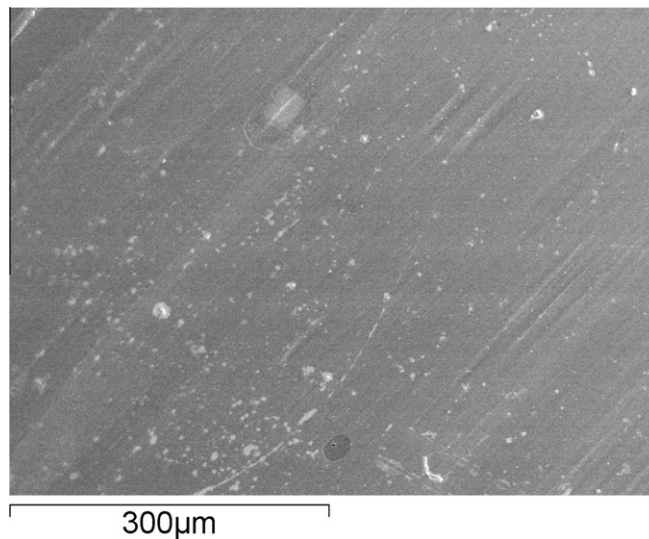
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**Figure 1.** DSC results for three single crystals of ammonium perchlorate. Linear heating until complete decomposition with a heating rate of 10 K/min. The maxima correspond to an exothermal effect.

(4.5:1.5 g) to give sample  $N[H/D]_4ClO_4$ . After each crystallization the deuterated product was filtered off and dissolved in a new solution of  $H_2O$  and  $D_2O$ .  $ND_4ClO_4$ : 20 g of  $D_2O$  was added to 5 g of 68 wt.% solution of  $DClO_4$ ; then 5.2 g of  $ND_4OD$  (25 wt.%) was added dropwise. The mixture was poured into a stoppered flask and placed in a refrigerator for 3 days. The crystalline product was filtered and dried. Crystals of  $NH_4ClO_4$  were prepared in the same way: 4.86 g of 70 wt.% solution of  $HClO_4$  in  $H_2O$  was used. Reagents: 68 wt.% solution of  $DClO_4$  in  $D_2O$ ,  $D_2O$  (99 atom% D), 25 wt.% solution  $ND_4OD$  in  $D_2O$  (Aldrich); 70 wt.% solution of  $HClO_4$  in  $H_2O$  (DDR); 25 wt.% solution  $NH_4OH$  in  $H_2O$  (POCH).

TG curves were registered with a TGA/SDTA851<sup>e</sup> apparatus (Mettler Toledo). The evolving gas was analyzed by on-line quadrupole mass spectrometry (QMS) with a Balzer GSD 300T apparatus. DSC curves were registered in Ar (80 ml/min) with a DSC821<sup>e</sup> Mettler Toledo apparatus.

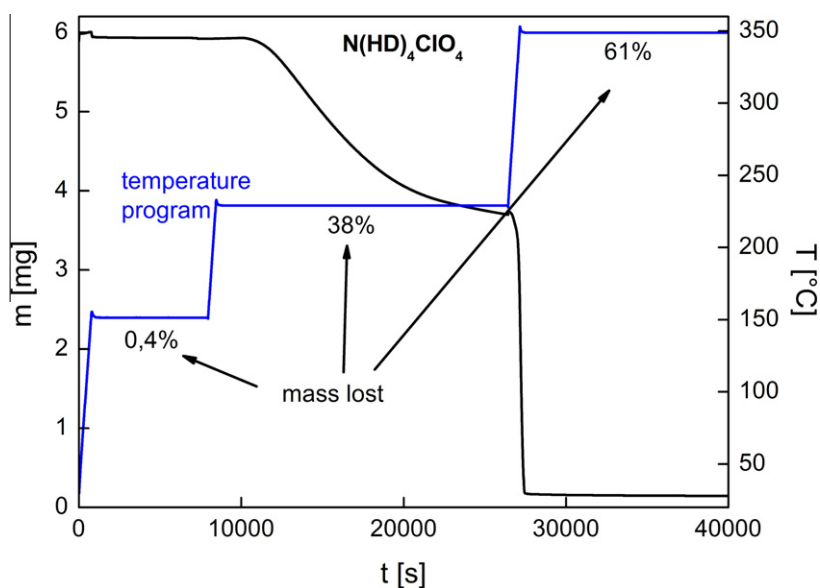


**Figure 3.** Secondary electron SEM image of a parent single crystal of  $N[H/D]_4ClO_4$ .

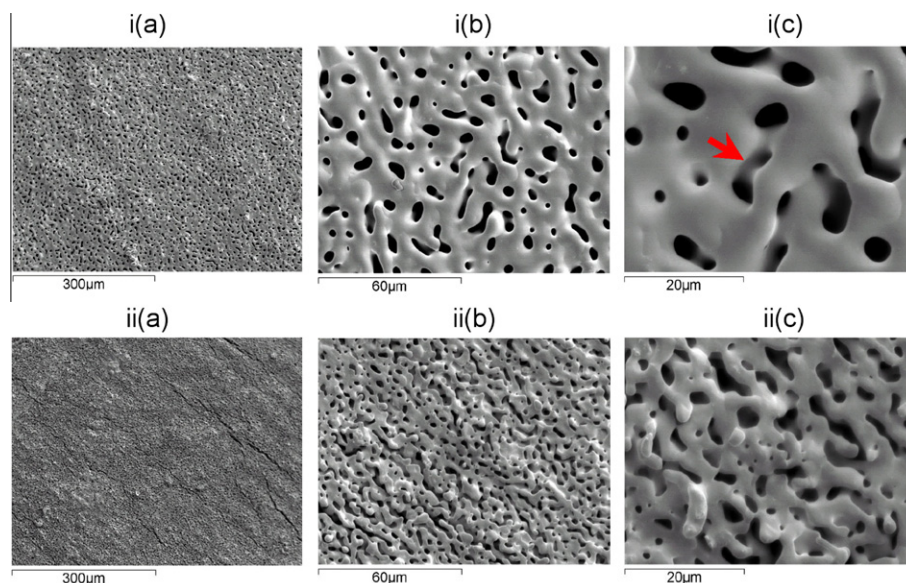
Secondary SEM images were obtained on a JEOL 5800 LV SEM operated at 15 kV. A 10 nm thin film of Au was evaporated onto the surface to reduce possible charging.

### 3. Results and discussion

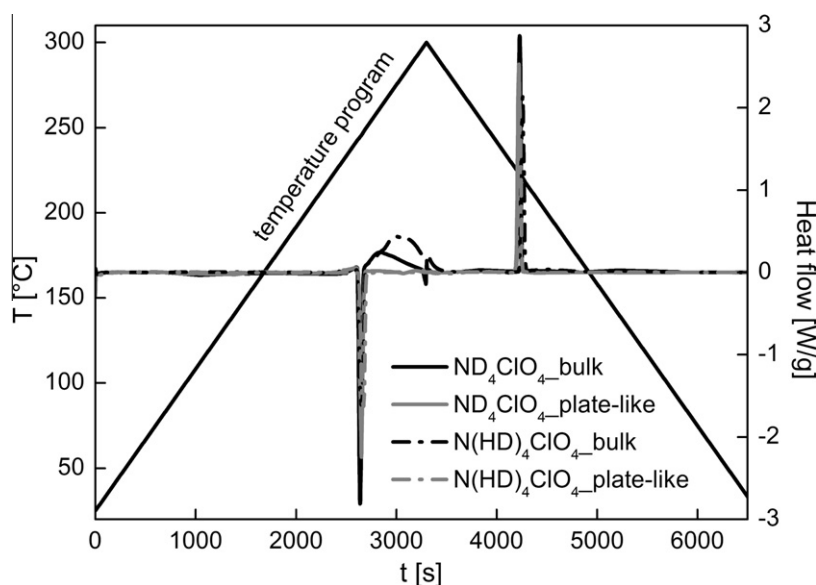
All parent single crystals were transparent. DSC shows (Figure 1) that all three samples undergo phase transition at the same temperature of ca. 240 °C. By contrast to the phase transition peaks, the reaction peaks do not coincide. Thermal decomposition is retarded for  $ND_4ClO_4$  but accelerated in the case of  $N[H/D]_4ClO_4$  in comparison with  $NH_4ClO_4$ . The partly deuterated sample is the most reactive of the three. The splitting of the low maximum, unlike in isotopically pure compounds, probably reflects the statistical occurrence of ammonium isomers (as recently discussed for partly deuterated ammonium hexachloroplatinate in [16]). Samples with



**Figure 2.** TG results for single crystal of  $N[H/D]_4ClO_4$  subjected to stepwise thermal treatment.



**Figure 4.** Secondary electron SEM images, at three different magnifications, of porous deuterated samples prepared at 230 °C: (i)  $\text{ND}_4\text{ClO}_4$ , (ii)  $\text{N}[\text{H}/\text{D}]_4\text{ClO}_4$ . For SEM images for  $\text{NH}_4\text{ClO}_4$  see [12].



**Figure 5.** DSC results for porous samples of ammonium perchlorate. Linear heating and cooling.

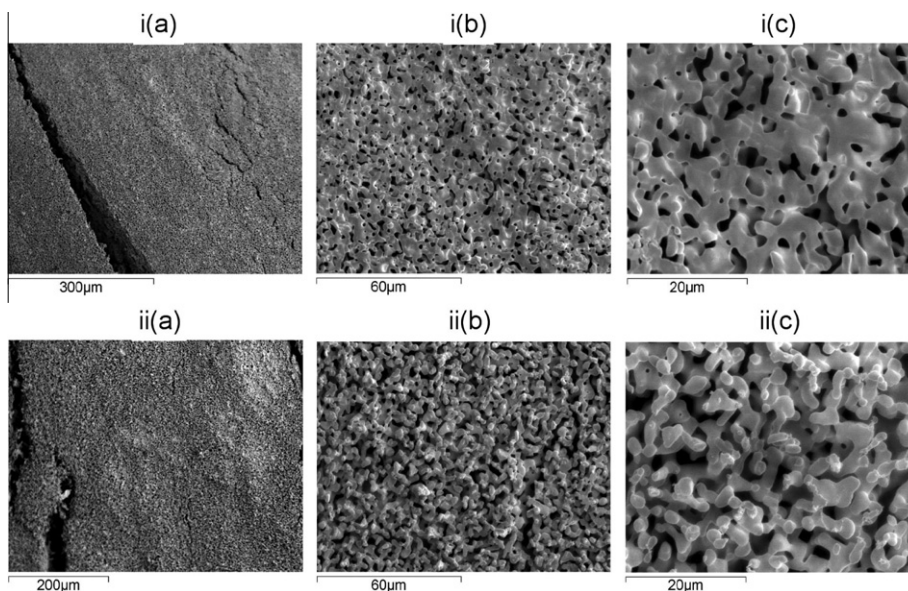
different H/D ratios need to be studied to elucidate this subtle point.

Figure 2 shows TG results for  $\text{N}[\text{H}/\text{D}]_4\text{ClO}_4$  with a stepwise temperature programme 150 → 250 → 350 °C. At 150 °C the sample is stable and no reaction occurs apart from water loss. At 230 °C thermal decomposition proceeds up to constant mass giving a porous product. At 350 °C the porous product is completely decomposed into gaseous species. The degree of conversion at 230 °C is 38%. No more than 33.5% conversion is found for completely deuterated samples, showing that  $\text{N}[\text{H}/\text{D}]_4\text{ClO}_4$  samples are more porous. This is confirmed by SEM examination. QMS registered simultaneously with TG shows that  $\text{N}_2\text{O}$  and NO are evolved during both low-temperature and high-temperature decomposition.  $\text{N}_2\text{O}$  is associated

with low-temperature decomposition and NO with high-temperature decomposition [9].

SEM images of original crystals show that the surface is nearly perfect except for some local mechanical damage. Figure 3 shows a fragment of a crystal face of  $\text{N}[\text{H}/\text{D}]_4\text{ClO}_4$ . The image of  $\text{ND}_4\text{ClO}_4$  is similar.

Porous samples for SEM examination were prepared by heating plate-like crystals in the DSC apparatus at 230 °C for 5 h to ensure constant mass. SEM images at different magnifications (Figure 4) show that nearly circular holes are formed in both deuterated samples. The different diameters of the holes indicate that decomposition does not start at the same time everywhere inside the crystal. When two circular holes are close, they begin to coalesce (arrow in



**Figure 6.** Secondary electron SEM images, at three different magnifications, of the samples shown in Figure 4 subjected to DSC linear heating and cooling: (i)  $\text{ND}_4\text{ClO}_4$ , (ii)  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$ .

Figure 4i-c) forming randomly oriented elongated holes. The surface of  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$  is less uniform showing cracks with the same orientation (Figure 4ii-a). The diameters of pores are smaller and so is the variance of pore diameters, indicating that the pores form within a shorter time. The concentration of the pores is higher. Finally, the crystal surface is covered with a deposit making it difficult to quantify the concentration of the pores, since some of them are obscured.

To confirm that the porous samples are composed of ammonium perchlorate, we have carried out DSC measurements using the temperature programme  $25^\circ \rightarrow 300^\circ \rightarrow 25^\circ \text{C}$  (heating rate  $\beta = 5 \text{ K/min}$ ) which covers the temperature of the phase transition (Figure 5). In addition to two plate-like porous samples shown in Figure 4, deuterated bulk porous samples have been treated in the same way. Phase transition is reversible and occurs at exactly the same temperature for all four samples. Results for non-deuterated samples (not shown) are the same. Accordingly, in all cases we deal with crystalline, if porous, ammonium perchlorate. At the scale of the Figure, broad DSC peaks indicating thermal decomposition are clearly seen only for bulk samples. Bulk crystals generally show higher reactivity due to higher concentration of dislocation intersections. However, this observation is not unambiguous since reactivity depends on the interplay of many factors. Our results indicate that in most cases, but not always, bulk crystals are more reactive.

SEM measurements of porous samples carried out after the DSC study provide further information. A comparison of Figure 6 and 4 reveals two main differences. First, cracks appear not only in  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$  but also in  $\text{ND}_4\text{ClO}_4$ , and have a preferential orientation. Second, surfaces of both samples in Figure 6 are covered with some material and the images are less clear, whereas only the  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$  sample is covered (Figure 4). Since DSC shows no additional peaks, there are good grounds to think that the surface species is recrystallized ammonium perchlorate present in different amounts and morphology. In the completely deuterated sample it is more compact; in the partly deuterated sample it is less compact and more abundant. The surface ammonium perchlorate is probably produced by the rearrangement of the surface during phase transition via nucleation and growth. For the partly deuter-

ated sample it is also observed at lower temperatures (Figure 4ii-c), indicating that the surface of sample  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$  is more labile.

#### 4. Conclusions

The rate of thermal decomposition of partly deuterated samples is fastest in the sequence  $\text{N}[\text{H}/\text{D}]\text{ClO}_4 > \text{NH}_4\text{ClO}_4 > \text{ND}_4\text{ClO}_4$ . The corresponding degrees of conversion at which decomposition stops at  $230^\circ \text{C}$  with the formation of a porous product are  $38\% > 33.5\% > 31\%$ . So does the volume fraction of the pores. The surface of partly deuterated porous samples is covered by a powdery deposit which probably consists of recrystallized ammonium perchlorate. The amount of the deposit is noticeably larger than for  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$ , indicating that the surface of  $\text{N}[\text{H}/\text{D}]\text{ClO}_4$  is more labile. However, even in this case the low-temperature thermal decomposition begins at the intersection of dislocations within the crystal and not on the crystal faces.

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