



# Low-temperature thermal decomposition of large single crystals of ammonium perchlorate

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## Abstract

Similarities and differences in the thermal behaviour of deuterated and nondeuterated ammonium perchlorate provide insights into the mechanism of its thermal decomposition. Thermal decomposition of  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$  always begins in the bulk of the crystals. In both cases decomposition stops when the degree of conversion is about 30%, giving porous products which undergo the same phase transition as the parent single crystals. Thermal decomposition of the deuterated sample is slower, the volume fraction of pores appears to be lower and the sample has a small quantity of ‘snow’ on the surface. These effects are best rationalized as caused by proton transfer at the intersections of dislocations in the bulk of the crystals.

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## 1. Introduction

Despite much research on various aspects of the thermal decomposition of ammonium perchlorate (see [1–7] and references therein), key aspects of the mechanism of the process remain controversial. One of these is the formation of a porous product upon low-temperature thermal decomposition of the orthorhombic phase. This curious feature, known since 1955 [8], is now of additional interest in the context of the interdisciplinary field on growth and form, as an insight into common features of porous solids. Another controversial question is the nature of the first

step in thermal decomposition. Many of the experimental and theoretical studies reviewed in Ref. [1] favour the proton transfer hypothesis. However, recent *ab initio* MD simulation indicated no proton transfer in the ideal crystal structure [3,4].

Progress in resolving these interrelated questions may be made by comparing the thermal behaviour of conventional and deuterated samples. The literature on thermal decomposition of deuterated ammonium perchlorate is fairly limited, and to the best of our knowledge there are no recent studies of large single crystals. We present here comparative SEM, DSC, TG and QMS results for deuterated and non-deuterated samples.

## 2. Methods

Parent single crystals were prepared as follows.  $\text{ND}_4\text{ClO}_4$ : 20 g of  $\text{D}_2\text{O}$  was added to 5 g of 68 wt% solution of  $\text{ND}_4\text{OD}$ ; then 5.2 g of  $\text{ND}_4\text{OH}$  (25 wt%) was added

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slowly; 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  $\text{NH}_4\text{ClO}_4$  were prepared in the same way: 4.86 g of 70 wt% solution of  $\text{HClO}_4$  in  $\text{H}_2\text{O}$  was used. Reagents: 68 wt% solution of  $\text{DClO}_4$  in  $\text{D}_2\text{O}$ ,  $\text{D}_2\text{O}$  (99 atom % D), 25 wt% solution  $\text{ND}_4\text{OD}$  in  $\text{D}_2\text{O}$  (Aldrich); 70 wt% solution of  $\text{HClO}_4$  in  $\text{H}_2\text{O}$  (DDR); 25 wt% solution  $\text{NH}_4\text{OH}$  in  $\text{H}_2\text{O}$  (POCH).

TG curves were registered with a TGA/SDTA851<sup>c</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>c</sup> Mettler Toledo apparatus.

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

The parent single crystals were transparent. Fig. 1a shows crystals of the deuterated ammonium perchlorate. Porous samples were prepared by the isothermal decomposition of single crystals at 230 °C and 250 °C (below and above phase transition temperature) until constant mass in the TG instrument with the registration of QMS signals for characteristic species. The photograph of the intermediate sample (Fig. 1b) clearly shows that thermal decomposition begins inside the crystal, not at crystal faces: the interior is white whereas the near-edge regions are still transparent. The mass loss is about 30% in both cases. The final porous product is white (Fig. 1c).

Fig. 2 shows combined TG and QMS results for the deuterated sample for a stepwise temperature program; the picture for the non-deuterated sample is similar. At 150 °C the sample is stable: nothing has happened except water loss. At 250 °C thermal decomposition leads to constant mass and the formation of a porous product.

The mass loss in non-deuterated and deuterated samples is 33.5% and 32%, respectively. At 350 °C the porous product is completely decomposed. The QMS lines from  $\text{N}_2\text{O}$  and  $\text{NO}$  recorded for the same sample at different temperatures show that, contrary to previous reports, the main products of decomposition are not  $\text{N}_2\text{O}$  and  $\text{NO}$  at low and high-temperatures, respectively [1]. The decomposition

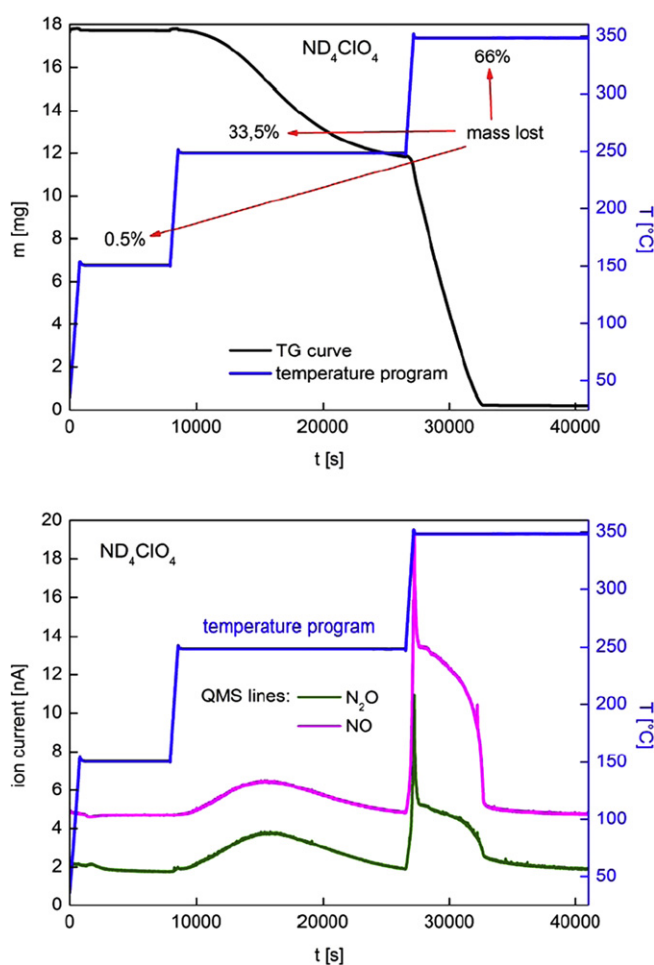


Fig. 2. TG and QMS results for single crystals of deuterated ammonium perchlorate subjected to stepwise thermal treatment.

products are the same, but at lower temperatures the reaction proceeds inside the crystal and the QMS peaks are smooth because of the desorption and transport of gaseous species from the bulk of the porous sample formed. At higher temperatures the reaction proceeds at the surface and gives sharp QMS peaks. The same is true for the QMS lines of other species.

Fig. 3 shows high-resolution SEM images of porous  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$ . The observed patterns are clearly different. The deuterated sample looks less indented and has a small quantity of 'snow' on the surface. The density

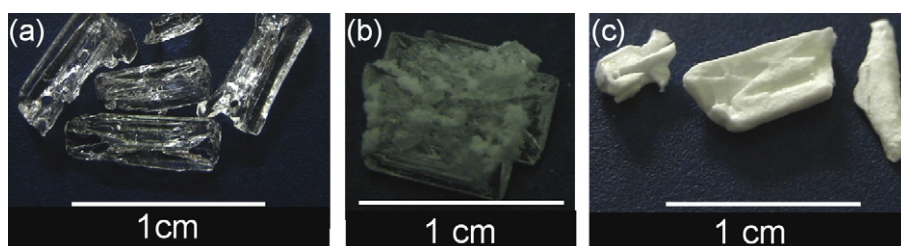


Fig. 1. Single crystals of deuterated ammonium perchlorate: (a) before thermal treatment, (b) after 1 h of thermal treatment, (c) after thermal treatment to constant mass at 230 °C.

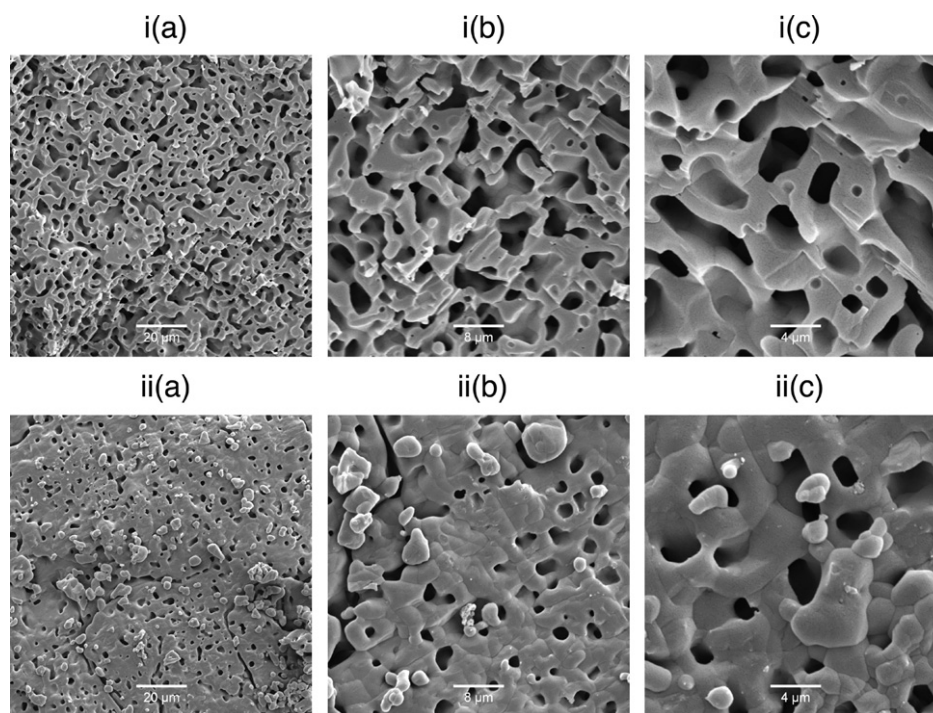


Fig. 3. Secondary electron SEM images, at three different magnifications, of porous samples prepared at 230 °C: (i)  $\text{NH}_4\text{ClO}_4$ , (ii)  $\text{ND}_4\text{ClO}_4$ .

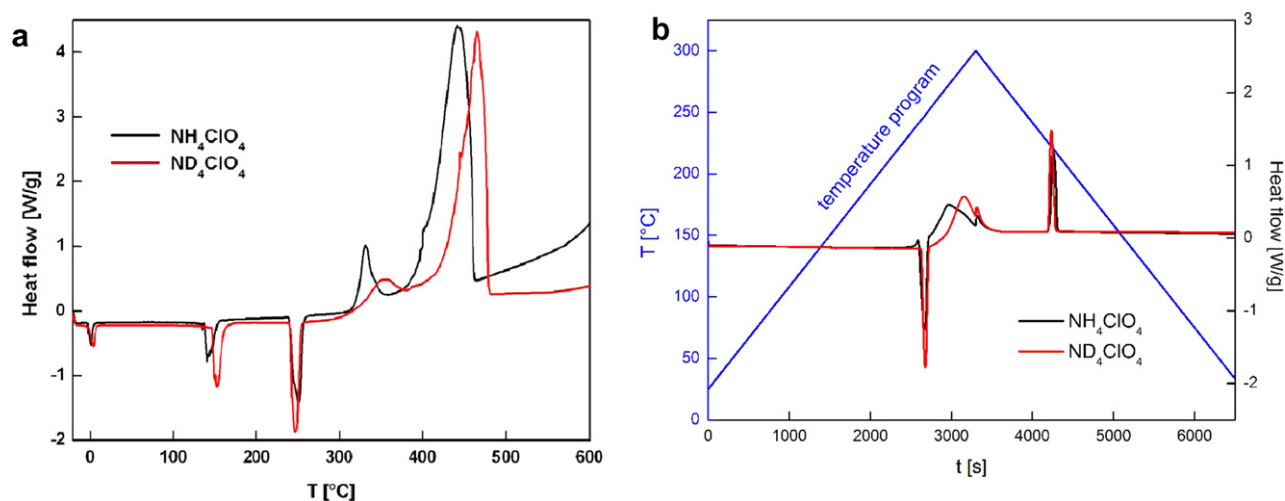


Fig. 4. DSC results for ammonium perchlorate: (a) linear heating of parent single crystals to complete decomposition, (b) linear heating and cooling of porous samples without decomposition.

of the holes is in the  $10^7$ – $10^8$   $\text{cm}^{-2}$  range, in agreement with the density of dislocations reported for single crystals of ammonium perchlorate [9]. DSC curves registered for porous samples (Fig. 4b) provide an insight into the nature of the material. There is a distinct phase transition at the same temperature of ca. 240 °C for all samples. The phase transition is reversible and as sharp as that for the parent crystals (Fig. 4a). This proves that the crystal structure of the porous sample is substantially preserved.

In contrast to the phase transition peaks, the reaction peaks for deuterated and nondeuterated samples are not coincident: the former is retarded as shown both in Fig. 4a and b. This is an additional argument in favour of proton transfer as the first reaction step.

Fig. 5a shows the immediate neighbourhood of the ammonium ion in the crystal structure [10,11] composed of seven perchlorate ions. From 28 oxygen atoms, ten are 2.9–3.2 Å from the nitrogen atom. These ten atoms, shown

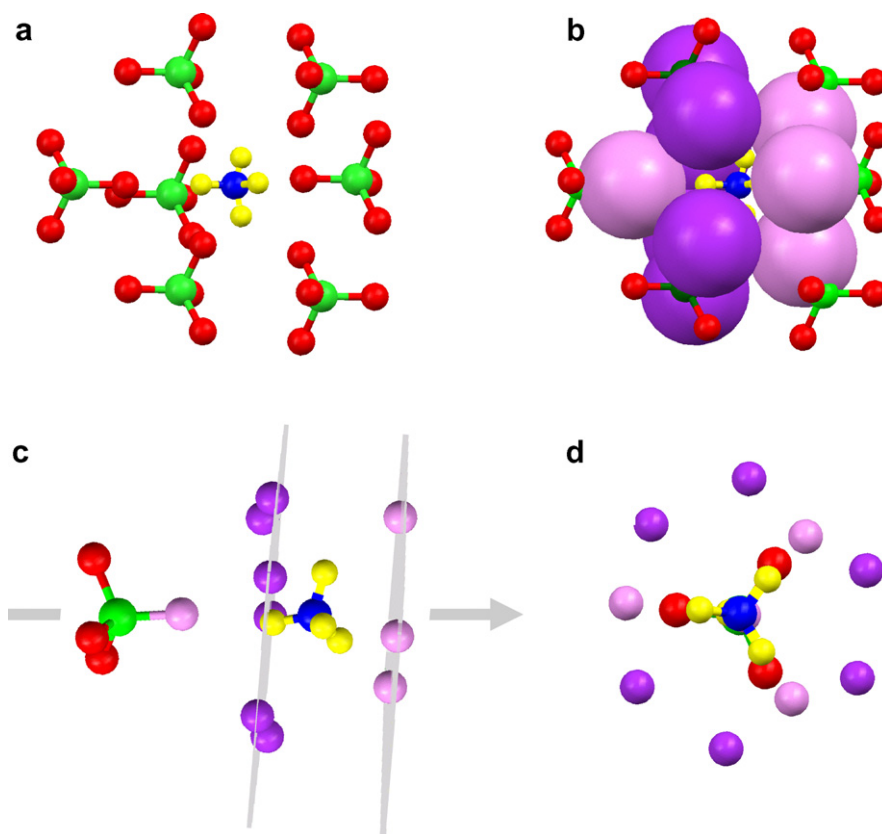


Fig. 5. The vicinity of the ammonium ion in the ideal crystal structure.

in Fig. 5b, fall into two groups. Four belong to different perchlorate ions (violet) and the remaining six to three perchlorate ions (two to each, purple<sup>1</sup>). These ten oxygen atoms form a comfortable cavity for the ammonium ion. Some of its peculiarities became clearer after removing chlorine atoms and most of the distant oxygen atoms (Fig. 5c). It appears that all purple oxygens lie practically in the same plane, which is nearly parallel to the plane formed by three violet oxygens (the angle between planes is 8.5°). The ammonium ion is situated between these planes. Fig. 5d shows the view along the axis indicated in Fig. 5c. For symmetry reasons (confirmed by our preliminary quantum chemical computations), this structure is favourable for rotation about the indicated axis but not for proton transfer. This agrees with results of *ab initio* MD calculations [3,4]. However, order is destroyed in the vicinity of dislocations.

#### 4. Conclusions

Thermal decomposition of  $\text{NH}_4\text{ClO}_4$  and  $\text{ND}_4\text{ClO}_4$  always begins inside the crystals, not on their faces. In both cases it stops when the conversion is about 30%, giving porous products which undergo the same phase transition

<sup>1</sup> For interpretation of color in Fig. 5, the reader is referred to the web version of this article.

as the parent single crystals. Thermal decomposition of the deuterated sample is slower, the volume fraction of pores appears to be lower and the sample has a small quantity of ‘snow’ on the surface. These effects are best rationalized as caused by proton transfer at the intersections of dislocations in the bulk of the crystals.

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#### References

- [1] V.V. Boldyrev, *Thermochem. Acta* 443 (2006) 1.
- [2] G.B. Manelis, G.M. Nazin, Yu.I. Rubtsov, V.A. Strunin, *Thermal Decomposition and Combustion of Explosives and Propellants*, Taylor & Francis, London, 2003.
- [3] L. Rosso, M.E. Tuckerman, *Solid State Ionics* 161 (2003) 219.
- [4] L. Rosso, M.E. Tuckerman, *Pure Appl. Chem.* 76 (2004) 49.
- [5] D.A. Lucca, M.J. Klopstein, O.R. Mejia, L. Rossetini, L.T. DeLuca, *Mater. Sci. Technol.* 22 (2006) 396.
- [6] R.S. Zhu, M.C. Lin, *Theoret. Comput. Chem.* 13 (2003) 373.
- [7] A.J. Lang, S. Vyazovkin, *Comb. Flame* 145 (2006) 779.
- [8] L. Bircomshaw, B. Newman, *Proc. Roy. Soc. A* 227 (1955) 228.
- [9] A.V. Raevskiy, in: *Mechanism of Thermal Decomposition of Ammonium Perchlorate*, G.B. Manelis (Ed.), Chernogolovka, 1981, p. 30 (in Russian).
- [10] C.S. Choi, H.J. Prask, E. Prince, *J. Chem. Phys.* 61 (1974) 3523.
- [11] J.-O. Lundgren, *Acta Cryst B* 35 (1979) 1027.