High-temperature behaviour of ammonium dihydrogen phosphate

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Abstract. For over five decades, the high-temperature behaviour of ammonium dihydrogen phosphate, NH₄H₂PO₄, has been a controversial subject; while initial works associate ionic conductivity increase around Tt=153°C to a physical transformation (structural phase transition), later research supports the chemical nature of the transformation. However, currently, the origin of the ionic conductivity increase is still not clear. To provide a possible interpretation for this phenomenon, a careful high-temperature thermal examination of this acid salt was conducted by means of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Mass Spectroscopy (MS). The results show that when this acid salt is heated through Tt, a chemical decomposition into phosphoric acid (H₃PO₄) and ammonia (NH₃) takes place. Considering that H₃PO₄ exhibits conductivity values around 10⁻³ S cm⁻¹, our results suggest that the conductivity increase observed at around Tt is an exclusive consequence of the presence of this decomposition product.

1. Introduction
Ammonium dihydrogen phosphate, NH₄H₂PO₄ (ADP), has been widely studied because of its several technological applications. For instance, owing to its high efficiency of nonlinear conversion and wide optical transparency region, this compound has been used in short-wavelength laser technology, as well as in nonlinear and integrated optics [1,2]. Other applications include using ADP in electrochromic devices and long-term retardants [3-5]. Furthermore, it is known that ADP belongs to the KDP-family compounds, with general formula MH₂PO₄ (M=Na, K, Rb, Cs, NH₄). These acid salts are dielectric crystals with hydrogen bonds. Under certain conditions, hydrogen ions can diffuse or hop by various mechanisms over the entire structure of these materials, due to excess proton positions [6]. Those compounds have been suggested for fuel cell applications because, upon heating, a superionic phase transition is observed [7-9]. However, the exact nature of the transformation leading to the “superprotonic phase” is still not clear and has been debated by many researchers [10-17].

The high-temperature behaviour of ADP is not free of controversy. Even though the conductivity increase around Tt has been observed by several authors [6, 18-23], some relate it to a structural phase transition [19-21], while others attribute it to a decomposition process [6, 18, 22-24]. Moreover, those who propose a chemical transformation disagree amongst themselves. For example, while Torijano et al. [22] and Lim and Lee [24] propose the chemical decomposition into diammomium dihydrogen diphosphate, (NH₄)₂H₂P₂O₇, and water (equation (1)), Abdel-Kader et al. [18] and Cheng et al. [23] suggest decomposition into ammonia, NH₃, and phosphoric acid, H₃PO₄ (equation (2)).
\[
2NH_4H_2PO_4(s) \rightarrow (NH_4)2H_2P_2O_7(s) + H_2O(v) \\
NH_4H_2PO_4(s) \rightarrow NH_3(v) + H_3PO_4(l)
\]  

(1)  

(2)

Here, \(s\), \(v\), and \(l\) denote solid, vapour and liquid state, respectively. Currently, the true nature of the transformation leading to the ADP conductivity increase, around \(T_t\), remains unclear. This work seeks to shed light on the high-temperature behaviour of ADP and its relation with this conductivity jump at around this temperature.

2. Experimental details

Ammonium dihydrogen phosphate pure crystals (99.99%) were purchased from Sigma Aldrich. Differential scanning calorimetry measurements were carried out by using a TA Instruments, DSC 2920. The sample was heated from room temperature to 430°C, at a heating rate of 1°C min\(^{-1}\). Ultra-pure argon was used as purge gas (50 mL min\(^{-1}\) flux). Temperature, baseline, and heat flow were carefully calibrated. A simultaneous TG-MS experiment was made by coupling a QMS BALZER ThermoStar\textsuperscript{TM} equipment to a TA Instruments TGA 2920 apparatus. The purge gas (90 mL min\(^{-1}\) flux) and the heating rate were the same as used on the DSC experiment. The DSC and TG-MS experiments were controlled (and their respective data recorded) by using Universal Analysis and Quadstar software. Even though the TG signal was recorded up to 600°C, the MS data was limited to our temperature range of interest. All the MS parameters as well as the TG mass and temperature were also carefully calibrated. Platinum pans were used for all experiments.

3. Results and discussions

Figure 1 shows the thermal analysis results for two ADP samples. Upon heating, a DSC endothermic anomaly is registered with onset and peak temperatures of 153.8 and 188.9°C, respectively. This result is consistent with previous reports [18-20], where a sharp conductivity increase at 157°C is observed [21]. However, our DSC peak temperature does not coincide with that reported by Cheng et al. [23] at 200°C. It should be taken into account that the heating rate used by these authors was higher (2.5°C min\(^{-1}\)) than that used in our study. This difference between the DSC peak temperatures of these measurements might be understood if the nature of the transformation is assumed as chemical (instead of physical). It is known that any chemical thermal decomposition is a time-dependent phenomenon. That is, a higher heating rate means higher onset decomposition temperature. Moreover, notice that before and after the DSC endothermic anomaly a sequence of very small anomalies is detected. Furthermore, the DSC anomaly does not correspond to a single well-defined peak, as typical for a physical transformation. Therefore, even though some researchers [19-21] attribute the conductivity increase to a structural phase transition, we support the hypothesis that when ADP is heated through \(T_t\), a chemical transformation takes place.

To better understand this transformation, a simultaneous TG-MS experiment was carried out to evaluate the proposed hypothesis. To our knowledge, this is the first time that a simultaneous TG-MS experiment on ADP is reported. Figure 1 shows its respective TG-DTG results. Even though from the TG curve only two major weight loss events are observed, the corresponding DTG curve shows three peaks. The DTG onset and peak temperatures of the first peak are 153.9 and 188.1°C, respectively. The two additional DTG peak temperatures are 270.8 and 520.5°C, correspondingly. The TG thermogram also shows that weight is practically zero at 530°C, indicating that the sample totally decomposes into gaseous products at this temperature.

Thus, considering the coincidence between the DSC (153.8 and 188.9°C) and DTG (153.9 and 188.1°C) onset and peak temperatures of the first thermal event, we believe that the endothermic anomaly that starts around \(T_t=153°C\) is an exclusive consequence of a chemical thermal decomposition process, rather than a structural phase transition.
Figure 1. DSC and TG (and its respective DTG curve) thermograms for ADP crystals. The high DSC temperature limit was fixed at 430°C because our main interest is the thermal anomaly associated to the conductivity increase. The heating rate was fixed at 1°C min⁻¹.

To examine which of the proposed thermal decomposition equations takes place, we need to know which molecule evolves when the weight loss occurs. According to the TG thermogram in Figure 1, the first DTG peak offset temperature is 250°C. Here, the weight loss corresponds to 15%. Consistent with the stoichiometry of equation (1), the total water evolution requires a mass loss of 7.8%, which corresponds to almost half of the mass loss measured in our experiment. On the other hand, for the respective stoichiometry of equation (2), the total ammonia evolution requires a mass loss of 14.8%. This value matches better with our TG measurement than that expected by equation (1). Therefore, the TG result suggests that ammonia (instead of water) evolves from the sample, by following equation (2). To confirm this last statement, our TG-MS results (for the 100-250°C temperature range) are shown in Figure 2. For comparison purposes and Figure clarity, only the DTG curve is shown together with the MS results. As seen from the m/z=14 (N⁺), 15 (NH⁺), 16 (NH₂⁺), and 17 (NH₃⁺) ionic current signals, peaks were detected at 188.4, 188.4, 188.6, and 188.7°C, respectively. Although the m/z=15 signal seems to have no peak, upon zooming (as shown in the insert) a well-defined peak is observed. From this Figure, it is evident the coincidence among all the MS peak temperatures. Also, those peaks coincide with the DTG peak temperature. Besides, the relative intensity of the MS peaks matches correctly with the mass spectrum of ammonia. Therefore, we conclude that when ADP is heated through T_r=153°C, a decomposition process starts, reaching the maximum decomposition rate at 188.1°C, according to equation (2).

Although Harris and Vela [6] and Cheng et. al. [23] also observed ammonia evolution when ADP is heated through 157°C, they did not use the TG-MS technique, which offers accurate results. In addition, through optical observation on the DSC cell, we found that at temperatures above 160°C, a liquid film coats the sample, as reported by Cheng et. al. [23]. If this transformation were a structural phase transition, there is no reason to see this liquid film. Moreover, it is known that if a sample

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undergoes a solid-solid phase transition, its mass must remain constant, but this is not the present case. Considering that phosphoric acid exhibits high conductivity values, around $10^{-3}\text{S}\cdot\text{cm}^{-1}$ [25], we believe that the ADP conductivity jump observed at 157°C [21] is exclusively related to the phosphoric acid production.

![Figure 2](image)

Figure 2. Simultaneous TG-MS (specifically DTG-MS) thermogram of an ADP crystal, at the temperature range 100-250°C. The insert magnifies the m/z=15 signal. The heating rate was fixed at 1°C min$^{-1}$.

It has been proposed that all the KDP-family compounds follow a similar decomposition kinetic process [13, 24]. According to this statement, upon heating, these acid salts decompose into water and a solid polymeric material, equation (3):

$$nM\text{H}_2\text{RO}_4(s) \rightarrow Mn\text{H}_2\text{RnO}_3n + 1(s) + (n - 1)\text{H}_2\text{O}(\nu), n \geq 1$$  \hspace{1cm} (3)

where M=Na, K, Rb, Cs, NH$_4$; $s$, $\nu$ mean solid and vapour states; and $n$ stands for the number of reactant molecules. However, according to our results, ADP is the KDP-family compound exception because instead of water and a polymeric product, ammonia and a liquid acid are the decomposition products. Consequently, the charge carrier in ADP does not correspond to the H$_2$O$^+$ ion, as proposed by Ortiz et al. [12,17] for the KH$_2$PO$_4$ and CsH$_2$PO$_4$ cases. Rather, it is explained in terms of the dissociation of phosphoric acid [25]. Despite this difference, upon heating, all the KDP-family compounds undergo a chemical transformation at the same temperature in which a physical transformation has been reported. For instance, Ortiz et al. [12,17] presented evidence that the tetragonal$\rightarrow$monoclinic structural phase transition in KH$_2$PO$_4$, and the low proton conduction$\rightarrow$superprotonic conducting phase transition in CsH$_2$PO$_4$ observed at 180 and 230°C, respectively, do not exist; instead, they propose that the thermal and conductivity behaviours observed are exclusive consequence of a chemical transformation.
Returning to the TG thermogram in Figure 1, the second and third DTG peaks register offset temperatures of 350 and 530°C, respectively. Their corresponding partial weight losses are 10% and 75%. According to stoichiometric calculations, we believe that these weight loss events are related to the chemical decomposition of phosphoric acid into pyrophosphoric acid and water; and then pyrophosphoric acid into methaphosphoric acid and water, respectively, as suggested by Abdel-Kader et al. [18].

4. Conclusions
The ADP high-temperature behaviour was carefully studied by means of DSC and simultaneous TG-MS. Upon heating, an endothermic anomaly was found with onset and peak temperatures of 153.8 and 188.9°C, respectively. This thermal event is related to weight loss. Certainly, not only the DTG onset (153.9°C) and peak (188.1°C) temperatures match the respective DSC onset and peak temperatures, but also the DTG and DSC peak temperatures fit well with the 14 (N⁺), 15 (NH⁺), 16 (NH₂⁺), and 17 (NH₃⁺) ionic current signal peak temperatures at 188.4, 188.4, 188.6, and 188.7°C, respectively. These peaks, which fit the ammonia mass spectrum, indicate that at Tt=153°C ADP decomposes into phosphoric acid and ammonia, equation (2). We conclude that the conductivity increase observed is an exclusive consequence of the presence of phosphoric acid in the sample and not due to a structural phase transition [19-21] or to a chemical transformation leading to a polymeric material and water [22,24], as proposed.

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