Vibrational study and thermal behavior of dihydrogenotriphosphatetrihydrate of 4-aminobenzoic acid and its anhydrous new form fertilizer type NP

Mustapha Belhabra 1,*, Ismail Fahim 1, Azzedine Atibi 1,2, Khadija El Kababi 1,2, Ali Ouasri 3, Soufiane Zerrat 1, Malika Tridane 1,2, Mohammed Radid 1, and Said Belaaouad 1

1 Laboratoire de Chimie Physique des Matériaux LCPM, Faculté des Sciences Ben M’'sik, B. P. 7955. Bd Cdt Driss El Harti. Université Hassan II de Casablanca, Maroc
2 Centre Régional des métiers d’éducation et de formation Casablanca Anfa, Bd Bir Anzarane Casablanca, Maroc
3 Centre Régional des métiers d’éducation et de formation Rabat. Maroc

Abstract: Chemical synthesis methods and IR spectrometry studies are reported for an organic triphosphate (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O and its anhydrous new form NH₃C₆H₅COOH)₃H₃P₁₀. The hydrate compound (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O was synthetized by the ion-exchange resin method. The dehydration of (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O leads at 130°C to (NH₃C₆H₅COOH)₃H₃P₁₀ crystallizing in the triclinic system with space group P 1 (Z = 2) [a = 14.566(6) Å, b = 6.866 (1) Å, c = 6.445 (6) Å, α = 112.36 (3) °, β = 94.51 (1) °, γ = 95.94(7) °, and V = 587.98 (1) Å³]. Merit’s figures are M (10) = 91.9 and F (10) = 55.6 (0.0032, 56). Its thermal behavior and kinetic study were studied by using thermal analyses TGA and DTA techniques between 25 and 600°C.

Keywords: p-carboxyphenylammonium triphosphate; IR spectrometry; vibrational study; thermogravimetric and differential analyses (TGA–DTA); Kinetic; Ozawa; KAS.

Introduction

The p-carboxyphenylamine (4-aminobenzoic acid) considered as a biological molecule, has an anticoagulant and antioxidant properties. It exists naturally in foods; it is produced by essential symbiotic bacteria to metabolize constantly in the human body 1. The active sites of several biological systems have kind of hydrogen bonding in hybrid compound 2. Indeed, the crystal structures of 4-carboxyphenylammonium dihydrogen phosphate and 4-carboxyaminium hydrogen sulphate compounds have been recently studied 3,4. Furtherer, the p-carboxyphenylammonium dihydrogen-monophosphate monohydrate compound was found to consist of H₂PO₄ anions, water molecules and p-HOOC-C₆H₅-NH⁺ cations 5. In this structure, anions and cations are linked to each other through strong hydrogen bonds, formed by all H atoms covalently bonded to anions, nitrogen, carboxylic groups and water molecules. A three-dimensional complex network of hydrogen bonds ensures the cohesion of the ionic structure.

The literature contains numerous studies of solid materials containing the P₁₀ group like NH₃ErHP₁₀, CuNa₃P₁₀(OH)₁₂H₂O, CuNa₃P₁₀, MgNa₃P₁₀(OH)₁₂H₂O, MgNa₃P₁₀, NiNa₃P₁₀(OH)₁₂H₂O et NiNa₃P₁₀. 6-10 During a systematic investigation of triphosphates associated with organic matrices, the triphosphate trihydrate of para carboxyphenylammonium (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O was prepared by the method of ion-exchange resin 11 in our laboratory 12,13.

The present study reports on the chemical preparation, IR vibrational spectroscopy, thermal dehydration and decomposition by thermal analyses (TGA and DTA) of (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O. The total thermal dehydration of this compound leads to the corresponding anhydrous form, which is a new triphosphate of para carboxyphenylammonium (NH₃C₆H₅COOH)₃H₃P₁₀. The kinetic parameters of dehydration have been studied for the title compound. Indeed, (NH₃C₆H₅COOH)₃H₃P₁₀(OH)₃H₂O...
and (NH₄C₆H₄COOH)₃H₃PO₄ are binary organic fertilizers type NP (nitrogen and phosphorus) second generation and corrosion inhibitors. The two triphosphates associated with para carboxyphenylammonium reported in the present work are stable in the normal conditions of temperature and hygrometry.

Experimental

\[ \text{H₃P₃O₁₀} + 3\text{NH₄C₆H₄COOH} + 3\text{H₂O} \rightarrow (\text{NH₄C₆H₄COOH})₂\text{H₃P₃O₁₀.3H₂O} \]

The so-obtained solution was then slowly evaporated at room temperature until large prisms of (NH₄C₆H₄COOH)₃H₃PO₄.₃H₂O were obtained. The triphosphoric acid, H₃P₂O₁₀, used in this reaction was prepared from an aqueous solution of Na₃P₂O₁₀ passed through an ion-exchange resin ‘Amberlite IR120’ \(^1\). \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) is stable in the normal conditions of temperature and hygrometry. \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) was also obtained using the same method, by the hydrolysis of \( P₃O₁₀^3^- \) ion in aqueous solution (NH₄C₆H₄COOH)₃H₃PO₄.₁₀

The product resulting from the total thermal dehydration of \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) at 130°C, is a new anhydrous triphosphate of para carboxyphenylammonium \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} \). The reaction is the following:

\[ (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \rightarrow (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} + 3\text{H₂O} \]

(\(\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} \) is stable in the normal conditions of temperature and hygrometry. With the additional increase in temperature, \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} \) is decomposed by evolving NH₃ followed by CO₂.

Data Collection and Reduction

Thermal behavior. Coupled TGA-DTA thermal analyses were performed using the multimodule 92 Setaram Analyzer operating from room temperature up to 1400°C, in a platinum crucible, at various heating rates from 1 to 15°C/min.

Infrared spectrometry. The infrared spectra of the powdered samples of \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) and \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} \) were recorded in the range 4000-400 cm⁻¹ with a Perkin-Elmer IR 983G spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

Results and Discussion

Crystallographic Characterization

- \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) studied elsewhere \(^{12,13} \) crystallizes in the triclinic system with space group P₁ \((Z = 2)\) \( [a = 9.844(1) \text{ Å}, b = 13.086(4) \text{ Å}, c = 13.320(2) \text{ Å}; \alpha = 107.12(2)^°, \beta = 106.08(1)^°, \gamma = 97.87(2)^°, \text{ and } V = 1530(1) \text{ Å}^3] \).

- \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀} \) crystallizes in the triclinic system with space group P1 \((Z = 2)\) \( [a = 9.844(1) \text{ Å}, b = 13.086(4) \text{ Å}, c = 13.320(2) \text{ Å}; \alpha = 107.12(2)^°, \beta = 106.08(1)^°, \gamma = 97.87(2)^°, \text{ and } V = 1530(1) \text{ Å}^3] \).

Synthesis (\(\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \)

Single crystals of (\(\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O} \) were prepared by slowly adding dilute cyclotriphosphoric acid, \( \text{H₃P₃O₁₀} \), to an aqueous solution of para carboxyphenylammonium, \( \text{NH₄C₆H₄COOH} \), according to the following chemical reaction:

\[ \text{Synthesis (NH₄C₆H₄COOH)H₃P₃O₁₀.3H₂O} \]

Vibrational study

Vibrations analysis of \( \text{H₃P₃O₁₀}^{3-} \)

The anion dihydrogenotriphosphate \( \text{H₃P₃O₁₀}^{3-} \), supposed to be of symmetry group \( \text{C}_1 \), has 39 internal vibration modes \( [\Gamma_{\text{int}} = 39 \text{ A}^1 \text{ (IR, Raman)}] \). According to this hypothesis, the anionic modes of \( \text{(H₃P₃O₁₀)}^{3-} \) free are all active in Raman and Infrared thus should appear in the form of simple bands.

In the structure of \( (\text{NH₄C₆H₄COOH})\text{H₃P₃O₁₀.3H₂O}) \), space group P1 \((\text{Group of factors } \text{C}_1) \) \(^{16} \), \( (\text{H₃P₃O₁₀})^{3-} \) has a \( \text{C}_1 \) site symmetry. This implies that all anionic internal modes (Table 1) generally remain infrared and Raman assets in the crystal site group. Theoretically, the presence of two units per unit of formula \((Z = 2)\) doubles the number of cationic and anionic modes with \( \text{Ag} \) and \( \text{Au} \) symmetry in the group of factors \( \text{C}_1 \). In the crystal being centrosymmetric (\( \text{C} \), group factor), only \( \text{Au} \) insensitive modes are active in infrared. All modes of vibration are theoretically active in infrared and Raman. These anionic modes correspond mainly to the vibrations of the \( \text{PO}_4^{3-} \) and \( \text{P-O-P} \).
Table 1. Correlation table (C1----> C1) for the internal vibrational modes of (H3P2O10)3−.

<table>
<thead>
<tr>
<th>Point group : C1</th>
<th>Site group : C1</th>
<th>Factor group : C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 A’(Ra, IR)</td>
<td>39 A’(Ra, IR)</td>
<td>39 Ag (Ra)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39 Au (IR)</td>
</tr>
</tbody>
</table>

Vibrations analysis of 4-carboxyphenyl ammonium

The free 4-carboxyphenyl ammonium cation is assumed to be of C3v symmetry point group, and then has 48 internal vibrational modes described as \( \Gamma_{\text{int}} = 32A’ \) (IR, Ra) + 16 A’ (IR, Ra). According to this assumption, the cationic modes are all Raman and Infrared active and should appear as single bands. In the structure of (NH4)3C6H4(COOH)3H3P2O10.3H2O compound, of P1 space group (C1 factor group)\(^{16}\), 4-carboxyphenyl ammonium cations have C1 site symmetry. This implies that all cationic internal modes (Table 2) usually remain infrared and Raman active in the site group of the crystal. The presence of two motifs per formula unit (Z = 2) doubles theoretically the number of cationic modes having A\(_g\) and A\(_u\) symmetry in the factor group C\(_1\). It is concluded that all vibrational modes are theoretically infrared and Raman active. Due to the centro symmetry of the crystal, only the ungerade modes A\(_u\) are Infrared active for the cations.

Table 2. Correlation table (C1----> C1) for the internal vibrational modes of (NH4)3C6H4(COOH)\(^+\).

<table>
<thead>
<tr>
<th>Point group : C1</th>
<th>Site group : C1</th>
<th>Factor group : C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>32A’ (Ra, IR)</td>
<td>32 A’(Ra, IR)</td>
<td>48 Ag (Ra)</td>
</tr>
<tr>
<td>16 A” (Ra, IR)</td>
<td>16 A’(Ra, IR)</td>
<td>48 Au (IR)</td>
</tr>
</tbody>
</table>

The mainly crucial cationic vibration bands correspond principally to the vibrations of amino NH\(_3^+\), carboxyl groups and benzene ring. It is to note that the distribution of the internal vibrations modes for benzene group by developing the normal coordinate analysis has been carried out \(^{17}\). In its free state, the NH\(_3^+\) cation has C\(_3v\) symmetry with a pyramidal geometry; the corresponding normal vibrational modes are described as non-degenerative modes \([\nu_1(A_1), \nu_2(A_1)]\), and doubly degenerated \([\nu_3(E)\) and \(\nu_4(E)]\), which all active as well as in Raman and Infrared. In the 4-carboxyphenyl ammonium cation of C\(_1\) symmetry, all NH\(_3^+\) modes become non-degenerative, with A’ and A” symmetry as indicated above, and usually remain Infrared and Raman active. The COOH has 9 internal vibrations modes given by 3m-3, where m is the number of atoms in the group. These modes correspond to O-H stretching, C-O stretching, C=O Stretching, in-plane-rocking, in-plane bending of C=O, in-plane bending of C=O, in-plane-bending of OH, out-of-plane wagging, and out-of-plane torsion.

Infrared Spectra of hydrate and anhydrous compounds

The infrared spectra of (NH4)3C6H4(COOH)3H3P2O10.3H2O and (NH4)3C6H4(COOH)3H3P2O10 compounds, recorded the range 4000-400 cm\(^{-1}\), are given in Figures 1a and 1b. These compounds consist of NH\(_3^+\) groups, COOH; para-substituted benzene ring, H\(_3\)P\(_2\)O\(_{10}\), and 3H\(_2\)O in the case of hydrate compound.  

* NH\(_3^+\) vibrations: Generally, the antisymmetric and symmetric stretching modes of the NH\(_3^+\) group appear in the spectral region of 3200-2800 cm\(^{-1}\) spectral region; whereas the antisymmetric and symmetric deformations appear in the 1660-1610 cm\(^{-1}\) and 1550-1480 cm\(^{-1}\) regions, respectively. In the Infrared spectrum of the anhydrous compound, the \(\nu_3\) (NH\(_3^+\)*) stretching is observed as a medium band at 3230 cm\(^{-1}\). The \(\nu_2\) (NH\(_3^+\)*) stretching modes give a weak and broad band at 2880 cm\(^{-1}\) in the case of the anhydrous compound and a medium band at 2887 cm\(^{-1}\) for the hydrated compound. The remaining bands corresponding to wagging w(NH\(_3^+\)), twisting t((NH\(_3^+\)) and rocking \(\rho\) (NH\(_3^+\)) bending vibrations are assigned as indicated in Table 3.

* Carboxyl groups vibrations: Studying vibrational spectra of benzoic acid, Antony et al.\(^{18}\) assigned C=O, C-O stretching modes; C-O, C=O in-plane bending, OH stretching, rocking mode, torsion mode and wagging mode to band appearing respectively at 1745 cm\(^{-1}\), 1050 cm\(^{-1}\), 594 cm\(^{-1}\), 1804 cm\(^{-1}\), 3785 cm\(^{-1}\), 554 cm\(^{-1}\), 594 cm\(^{-1}\) and 441 cm\(^{-1}\). Florio et al.\(^{19}\) observed C=O stretching at 1752 cm\(^{-1}\), C-O stretching at 1347 cm\(^{-1}\), C-O in-plane bending at 628 cm\(^{-1}\), OH stretch at 3785 cm\(^{-1}\), rocking mode at 628 cm\(^{-1}\), and wagging mode at 160 cm\(^{-1}\). In the present study, the assignment of bands corresponding to the different COOH vibrations is shown in Table 3.
* Para substituted benzene ring vibrations: The C-H stretching modes of benzene ring are generally expected in the 3115-3005 cm\(^{-1}\) \(^{20, 21}\). The $\beta$(C-H) “in-plane” and $\delta$(C-H) “out-plane” bending vibrations are located in the range 1250-1000 cm\(^{-1}\) and 900-690 cm\(^{-1}\), respectively \(^{20, 22}\). For the studied compounds, the $\beta$(C-H) and $\delta$(C-H) of the benzene ring are observed in the expected ranges, as indicated in Table 3. The C=C and C–C benzene ring stretching modes occur in the 1650-1430 cm\(^{-1}\) and 1400-1300 cm\(^{-1}\), respectively \(^{20, 21}\). For the two compounds, these modes are assigned to the corresponding bands as illustrated in Table 3. Finally, the C-N stretching and the ring breathing modes were identified for the studied compounds and given in Table 3.

* $\text{H}_2\text{P}_2\text{O}_{10}^3$: vibrations: The assignment of bands due to the fundamental modes, valence and bending, of $\text{P}_2\text{O}_{10}^5$ anions are presented in Table 3 for both triphosphates. The frequencies of the $\text{P}_2\text{O}_{10}^5$ anion are assigned based on the characteristic vibrations of the P–O–P bond in the PO$_2$ and PO$_3$ groups. Since the P–O bond in the PO$_2$ and PO$_3$ group is weaker than that in the P–O–P Bridge, the vibrational frequencies of PO$_2$ and PO$_3$ are expected to be higher than those for P–O–P. The bands due to the symmetric and antisymmetric stretching frequencies of PO$_2$ and PO$_3$ in $\text{P}_2\text{O}_{10}^5$ are generally observed in the region 1190–1010 cm\(^{-1}\).\(^{22, 23}\) The bands observed in the domain 970–840 cm\(^{-1}\) are attributed to the antisymmetric and symmetric POP stretching modes. The bands due to $\delta$(PO$_3^-$) and $\delta$(POP) are also identified in Table 3, which contains the IR frequencies and the vibrational modes corresponding to Rb$_2\text{H}_2\text{P}_2\text{O}_{10}$.1.5H$_2$O, para-carboxyphenylammonium NH$_2$C$_6$H$_4$COOH, compared with those of (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$.3H$_2$O and (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$. The IR frequencies of the $\text{P}_2\text{O}_{10}^5$ anions observed in the two triphosphates associated to para carboxyphenlammonium, (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$.3H$_2$O and (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$, are the same as those observed in the triphosphate associated to rubidium Rb$_2\text{H}_2\text{P}_2\text{O}_{10}$.1.5H$_2$O.\(^{22}\)

![Figure 1](https://example.com/figure1.png)

**Figure 1.** IR spectra of the phosphates: (a) (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$.3H$_2$O and (b) (NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$_2$O$_{10}$

<table>
<thead>
<tr>
<th>Rb$_2$H$_2$P$<em>2$O$</em>{10}$.1.5H$_2$O</th>
<th>NH$_2$C$_6$H$_4$COOH</th>
<th>(NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$<em>2$O$</em>{10}$.3H$_2$O</th>
<th>(NH$_2$C$_6$H$_4$COOH)$_2$H$_2$P$<em>2$O$</em>{10}$</th>
<th>Vibrational modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>3553</td>
<td>3545</td>
<td></td>
<td></td>
<td>$\nu$ (OH)</td>
</tr>
<tr>
<td>3428</td>
<td>3466</td>
<td>3449</td>
<td></td>
<td>$\nu$as (NH$_3^+$)</td>
</tr>
<tr>
<td></td>
<td>3367</td>
<td></td>
<td></td>
<td>$\nu$as (NH$_2^+$)</td>
</tr>
<tr>
<td></td>
<td>3233</td>
<td>3230</td>
<td></td>
<td>$\nu$ (OH) + $\nu$ (C-H)</td>
</tr>
<tr>
<td></td>
<td>3065</td>
<td></td>
<td></td>
<td>$\nu$ (NH$_3^+$)</td>
</tr>
<tr>
<td></td>
<td>2980</td>
<td>2885</td>
<td>2880</td>
<td>Non-fundamental modes</td>
</tr>
<tr>
<td></td>
<td>2730</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2678</td>
<td>2614</td>
<td>2577</td>
<td></td>
</tr>
<tr>
<td>2350</td>
<td>2552</td>
<td>2390</td>
<td>2036</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>1912</td>
<td>1846</td>
<td>β C=O in-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1770</td>
<td>1673</td>
<td>1698</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1632</td>
<td>1614</td>
<td>1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1602</td>
<td>1578</td>
<td>1616</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1580</td>
<td>1550</td>
<td>1539</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1532</td>
<td>1510</td>
<td>1516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1441</td>
<td>1431</td>
<td>1468</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1420</td>
<td>1403</td>
<td>1424</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1321</th>
<th>1317</th>
<th>1341</th>
</tr>
</thead>
<tbody>
<tr>
<td>1293</td>
<td>1237</td>
<td>v C-C/ v C-N/ v C-O</td>
</tr>
<tr>
<td>1233</td>
<td>1180</td>
<td>1200</td>
</tr>
<tr>
<td>1203</td>
<td>1156</td>
<td></td>
</tr>
<tr>
<td>1191</td>
<td>1131</td>
<td>1130</td>
</tr>
<tr>
<td>1101</td>
<td>1096</td>
<td>1060</td>
</tr>
<tr>
<td>1032</td>
<td>1075</td>
<td>1000</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>934</td>
</tr>
<tr>
<td>920</td>
<td>899</td>
<td>883</td>
</tr>
<tr>
<td>843</td>
<td>773</td>
<td>761</td>
</tr>
<tr>
<td>714</td>
<td>709</td>
<td>727</td>
</tr>
<tr>
<td>684</td>
<td>686</td>
<td>678</td>
</tr>
<tr>
<td>618</td>
<td>637</td>
<td>540</td>
</tr>
<tr>
<td>555</td>
<td>542</td>
<td>498</td>
</tr>
</tbody>
</table>

**Study of the thermal behavior of (NH₄)₃P₃O₉**

To facilitate the thermal behavior study of (NH₄)₃P₃O₉, we firstly studied the decomposition of (NH₄)₃P₃O₁₀·3H₂O, which was prepared by the method of ion-exchange resin, and characterized crystallographically by M. Bagie-Bouechar in 1976. It crystallizes in the monoclinic system with space group P2₁/n (Z = 4, C₂h), and parameters: a = 11.515 Å, b = 12.206 Å, c = 7.699 Å, β = 101.63°. The structure of (NH₄)₃P₃O₁₀ was resolved using that of its isotype K₃P₃O₉. In this structure, the P₃O₉ cycle does not have proper symmetry. Its C₁ symmetry is approximately C₃ᵥ, where k⁺ cations or NH₄⁺ occupy three separate sites.

Indeed, we have prepared (NH₄)₃P₃O₉ by the exchange resin method and controlled its purity by X-ray diffraction, and then we examine the thermal behavior, between 25 and 1400°C (sample mass: 23 mg) using the coupled TG-DTA analyses with a heating rate of 1°C/min. TGA, DTA and DTG curves (Figures 2 and 3) show two distinct steps. The first step between 180°C and 450°C corresponds to a loss in brutal mass 17.5%. This loss is the equivalent of three ammonia molecules per formula unit. The DTG curve indicates two distinct peaks, the first at 180 °C and the second at 295°C. However, the elimination of the first molecule of NH₃ does not seem to be accompanied by a thermal effect. For the other two molecules of NH₃, the DTA curve indicates a peak, endothermic top temperature to 290°C, which is of asymmetrical profile. This confirms the existence of more than one type of site occupied by NH₄⁺ in the structure of (NH₄)₃P₃O₉. Moreover, explains the succeeding departure of 3 molecules of NH₃ because of distinct bond energies. At 450°C, after the departure of 3 ammonia molecules per formula unit and a thermal residue, 240 g/mol, destroyed (NH₄)₃P₃O₉ and leads to H₃P₃O₉. The reaction scheme is the following:
The second stage, between 450°C and 650°C, corresponds to a weight loss of 64.5%, the equivalent of 2/3 of the weight of thermal residue H₃P₃O₉. This loss is accompanied by an intense and endothermic DTA peak at 586°C due to the decomposition of the acid H₃P₃O₉ amorphous entity which releases H₂O and P₂O₅ with a top speed at 560°C on the DTG curve. At 650°C, the reaction scheme is the following:

\[
\text{H}_3\text{P}_3\text{O}_9 \rightarrow \text{HPO}_3\text{(amorphous)} + \text{H}_2\text{O} + \text{P}_2\text{O}_5
\]

Between 650°C and 1400°C, any mass loss was observed in the TGA thermogram, and any thermal effect was highlighted by the TGA-DTA thermograms (Figure 2).
Study of the thermal behavior of \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\)

The study of the thermal behavior of tetra(4-carboxyphenyl ammonium) dihydrogenotriphosphate trihydrate \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\), was performed by linear increase in temperature from 25 to 600°C using the TGA coupled on thermodifferential of powder samples of about 20 mg, at different heating rates: \(v = 1, 3, 6, 10\) and 15°C/min under atmospheric pressure.

**Thermogravimetric analysis**

The TGA thermograms of \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\), realized at different heating rates (Figure 4), have all the same look and show five separate mass loss steps. Careful examination of the thermograms, carried out at low speed, indicates that the first step is not on that initially the water whereas the other four steps are related to entities from the decomposition of the organic matrix and the mineral matrix.

The TGA-DTA thermogram realized at a heating rate of 3°C/min (Figure 5) shows 5 mass loss steps:

- The first stage begins at 110°C and ends at 126°C. It appears to involve a single process of evolving water (mass loss calculated 7.47%, observed 7.5%). The DTG thermogram has a maximum loss of water at 118°C.
- Between 126 and 168°C, in the TGA thermogram, there is no variation of mass.
- The second step starts at 168°C and ends at 188°C. It corresponds to a mass loss, relatively fast, about 7.01%. It is attributed to the loss of three molecules of ammonia for which the mass loss is theoretically calculated of 7.05%. The maximum loss is observed on the DTG thermogram at 179°C.
- The third stage, between 188 and 260°C, corresponding to a mass loss of 18.22%, is assigned to 3 moles of CO\(_2\) per formula unit (mass loss calculated 18.2%). Two loss maxima are reported on the DTG curve, during the third step, the first peak well pronounced at 197°C and a second peak doubtful to 214°C.
- The fourth step starts at 260 and ends at 310°C. It corresponds to a weight loss of 13.4% and could be attributed to the loss of gas from the decomposition of the organic matrix. The maximum rate of loss is observed on the DTG thermogram at 280°C.
- The fifth stage, between 310 and 530°C, corresponding to a mass loss of 20.9%. This loss could be attributed to the combustion of the organic matrix.

![Figure 4. TGA thermograms of \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\) at different heating rates.](image-url)
Figure 5. TG-DTG thermograms of \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\) at 3°C/min.

- The sixth stage, between 530 and 600°C, corresponding to a weight loss of 17%, is accompanied by a DTG peak at 567°C corresponding to the maximum speed of water \(\text{H}_2\text{O}\) and pentaoxide phosphorus \(\text{P}_2\text{O}_5\) release from the decomposition of the mineral matrix.

Differential thermal analysis

DTA thermograms made at different speeds and coupled with the thermogravimetric analysis are shown in Figure 6. The analysis of the thermogram corresponding to the heating rate 3°C/min (Figure 7) allows to highlight the following points:

The first phase, between 110 and 126°C, accompanied by an endothermic peak at 118°C, which coincides with the maximum reported loss on the derivative curve at 118°C. This peak corresponds to the loss of 3 water molecules according to the following reaction scheme:

\[
\text{(NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O} \rightarrow (\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10} + 3\text{H}_2\text{O}
\]

An exothermic peak was observed at 147°C only for the weak heating rates for 1 and 3°C/min after the total removal of water. It corresponds to the crystallization of the corresponding anhydrous \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}\). This well-crystallized phase was characterized by its IR spectrum (Figure 1).

- The second stage, between 168 and 188°C, is accompanied by two endothermic peaks at 174 and 180°C. The last peak at 180°C coincides with the maximum loss at 179°C. These two endothermic effects are attributed to the loss of three molecules of ammonia. The presence of two endothermic peaks may be interpreted based on structural data of \((\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}\), which indicates the presence of three types of nitrogen atoms. The first endothermic peak at 174°C, can be attributed to the departure of two mol molecules \(\text{NH}_3(1)\) and \(\text{NH}_3(3)\), the two nitrogen atoms having thermal agitation factors very close \(2^2\), and the second at 180 °C, the last remaining ammonia molecule \(\text{NH}_3(2)\) (having a nitrogen atom of thermal agitation factor low \(12^2\)). The reaction scheme is as follows:

\[
(\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10} \rightarrow (\text{C}_7\text{H}_5\text{O}_2)\text{C}_6\text{H}_5\text{H}_2\text{P}_3\text{O}_{10}\text{O}_2 + 3\text{NH}_3
\]

- The third stage, between 188 and 260°C, corresponding to the departure of 3 moles of \(\text{CO}_2\), is accompanied by an endothermic peak at 197°C which coincides with the maximum loss reported on the DTG curve peak at 197°C. It is worth noticing that this third stage can be subdivided into two distinct stages. The first one is made between 188 and 210°C, the second between 210 and 260°C. In this case, the endothermic peak observed at 197°C would be the \(\text{CO}_2\) group the more weakly bonded to the organic chain. The endothermic peak observed at 197 °C is related to the \(\text{CO}_2\) group, more weakly bonded to the organic chain \((\text{CO}_2(7))\), and it corresponds to the liberation of 6.06%, the \(\text{CO}_2\) removed between (1/3) 188 and 210°C (18.02%). The second stage from 12.1% per formula unit; (2/3) of \(\text{CO}_2\) corresponding to groups \((\text{CO}_2(14))\) and \((\text{CO}_2(21))\). Indeed, the structure of the compound shows that the \(\text{C}_6\)-\(\text{C}_7\) distance is relatively longer, 1.498Å longer, longer than 1.498Å. The reaction scheme in this step is as follows:

\[
(\text{C}_7\text{H}_5\text{O}_2)\text{C}_6\text{H}_5\text{H}_2\text{P}_3\text{O}_{10} \rightarrow (\text{C}_6\text{H}_3)\text{H}_2\text{P}_3\text{O}_{10} + 3\text{CO}_2
\]
The thermal residue obtained at the end of the third stage ($\text{C}_6\text{H}_5\text{H}_2\text{P}_3\text{O}_{10}$ after loss successively of $3\ \text{H}_2\text{O}$, $2\text{NH}_3$, $1\text{NH}_3$) and $3\ \text{CO}_2$ per formula unit undergoes thermal degradation of organic matrices and mineral. The ATD Thermogram brings up an exothermic peak at around $300^\circ\text{C}$, which could be attributed to an atomic reorganization. Indeed, the temperature of the start of the exothermic effect coincides with the onset temperature of the 4th stage and the exothermic peak observed at $300^\circ\text{C}$ corresponds to the temperature of the end of this step.

- The fifth stage, between $310$ and $530^\circ\text{C}$, makes appear an exothermic peak at the top temperature of $432^\circ\text{C}$, which may be due to the burning of the residue of the organic matrix.

**Figure 6.** TGA thermograms of ($\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}$ at different heating rates

**Figure 7.** TGA-DTA thermograms of ($\text{NH}_3\text{C}_6\text{H}_4\text{COOH})_3\text{H}_2\text{P}_3\text{O}_{10}.3\text{H}_2\text{O}$ at $3^\circ\text{C/min}$.

**Measurement of kinetic parameters**

Estimation of the thermodynamic functions:

Various equations of kinetic analyses are known $^{23-27}$. Ozawa and KAS methods are selected in studying the kinetics of thermal dehydration of the title compound. So, water loss kinetic parameters were evaluated from
the curves \( \ln(v/T^2m) = f(1/Tm) \) and \( \ln(v) = f(1/Tm) \) (Figures 8 and 9), where \( v \) is the heating rate and \( Tm \) the sample temperature at the thermal effect maximum. The characteristic temperatures at maximum dehydration rates, \( Tm \) in °C, at different heating rates from the DTA curves of \( (NH_3C_6H_7COOH)_3H_2P_2O_10\cdot3H_2O \) are gathered in Table 4.

**Table 4.** Temperatures of endothermic peak summits on the DTA curves of \( (NH_3C_6H_7COOH)_3H_2P_2O_10\cdot3H_2O \).

<table>
<thead>
<tr>
<th>Heating rates</th>
<th>1°C/min</th>
<th>3°C/min</th>
<th>6°C/min</th>
<th>10°C/min</th>
<th>15°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 H₂O</td>
<td>108</td>
<td>118</td>
<td>134</td>
<td>142</td>
<td>152</td>
</tr>
<tr>
<td>2 NH₃</td>
<td>161.4</td>
<td>174</td>
<td>189</td>
<td>193.4</td>
<td>206</td>
</tr>
<tr>
<td>1 NH₃</td>
<td>166.6</td>
<td>180</td>
<td>194</td>
<td>198</td>
<td>206</td>
</tr>
<tr>
<td>3 CO₂</td>
<td>181.6</td>
<td>197</td>
<td>216</td>
<td>219</td>
<td>233</td>
</tr>
</tbody>
</table>

From these temperatures, the apparent activation energies of dehydration were calculated for the \( (NH_3C_6H_7COOH)_3H_2P_2O_10\cdot3H_2O \). For the Kissinger-Akahira-Sunose (KAS) 26 method, the slope of the resulting straight line on the curve: \( \ln(v/T^2m) = f(1/Tm) \) (Figure 8), equals to:

\[-Ea/R \text{ allows the apparent activation energy to be calculated (Table 4). With reference to the Ozawa method, the slope of the resulting straight line on the curve: } \ln(v) = f(1/Tm) \text{ (Figure 9), equals to} -1.0516E/R, \text{ also allows the apparent activation energy to be calculated by this second way (Table 4). The equations used for the two methods are the following:}\]

For KAS:

\[ Ln \left( \frac{v}{T^2m} \right) = Ln \left( \frac{AR}{E} \right) - \frac{1}{Tm} \]

For Ozawa:

\[ Ln(v) = Ln \left( \frac{AR}{1.0516E} \right) - 1.0516 \left( \frac{E}{R} \right) \left( \frac{1}{Tm} \right) \]

The pre-exponential factor or Arrhenius constant (A) and the related thermodynamic functions can be calculated by using the activated complex theory (transition state) of Eyring 28-31. The following general equation can be written:

\[ A = \left( \frac{e^xk_BT_m}{h} \right) exp \left( \frac{\Delta S^*}{R} \right) \]

Where e is the Neper number (e = 2.7183), \( x \) is the transition factor, which is unity for the monomolecular reaction, \( k_b \) is the Boltzmann constant (\( k_b = 1.3806 \times 10^{-23} \) J K⁻¹), \( h \) is Plank’s constant (\( h = 6.6261 \times 10^{-34} \) J s), \( T_m \) is the peak temperature of the DTA curve, R is the gas constant (\( R = 8.314 \) J K⁻¹ mol⁻¹) and \( \Delta S^* \) is the entropy change of transition state complex or entropy of activation. Thus, the entropy of activation may be calculated as follows:

\[ \Delta S^* = RLn \left( \frac{Ah}{e^x k_BT_m} \right) \]

The enthalpy change of transition state complex or heat of activation \( (\Delta H^*) \) and Gibbs free energy of activation \( (\Delta G^*) \) of decomposition were calculated according to Eqs. (5) and (6), respectively:

\[ \Delta H^* = E^* - R T_m \]

\[ \Delta G^* = \Delta H^* - T_m \Delta S^* \]

Where, \( E^* \) is the activation energy \( E_a \) of both KAS 25 and Ozawa 26 methods. The values of the activation energy are gathered in (Table 5). Thermodynamic functions were calculated from Eqs. (4), (5) and (6) and summarized in (Table 6). The negative values of \( \Delta S^* \) from two methods for the dehydration step reveals that the activated state is less disordered compared to the initial state. These \( \Delta S^* \) values suggest a large number of degrees of freedom due to rotation which may be interpreted as a « slow » stage 30-33 in this step. The positive values of \( \Delta G^* \) at all studied methods are because, the dehydration processes are not spontaneous. The positivity of \( \Delta G^* \) is controlled by a small activation entropy and a large positive activation enthalpy according to the Eq. 6. The endothermic peaks in DTA data agree well with the positive sign of the activation enthalpy \( (\Delta H^*) \). The estimated thermodynamic functions \( \Delta S^* \) and \( \Delta G^* \) (equation 6, Table 6) from two methods are approximatively the same due to the same pre-exponential factor of about 10⁻¹². While \( \Delta H^* \) (equation 5, Table 6) exhibits, in all the cases, an independent behavior on the pre-exponential factor as seen from exhibiting nearly the same value.
shows the existence of ion channels H

(C

atriphosphate with a

P

aminobenzoic acid leads, due to the hydrolysis of

coupled spectrometry vibration and TGA

(NH

4

ammonium trihydrate

3

C

6

H

3

COOH)\textsubscript{3}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O

Conclusion

The structural and thermal study of 4-carboxyphenyl dihydrogenotriphosphate ammonium trihydrate (NH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}COOH)\textsubscript{3}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O developed by IR spectrometry vibration and TGA-DTA analyses coupled brings up the following results:

The reaction of phosphoric acid with aminobenzoic acid leads, due to the hydrolysis of P\textsubscript{3}O\textsubscript{8}\textsuperscript{4-} ion in aqueous solution or by using H\textsubscript{2}P\textsubscript{3}O\textsubscript{10} to a triphosphate with a formula (C\textsubscript{6}H\textsubscript{5}NO\textsubscript{2})\textsubscript{2}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O. The structural resolution shows the existence of ion channels H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}\textsuperscript{3-} linked together by hydrogen bonds. Organic cations, water molecules and phosphates chains are linked together by hydrogen bonds. A detailed vibrational study is reported for (NH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}COOH)\textsubscript{3}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O with all of its entities NH\textsubscript{3}, C\textsubscript{6}H\textsubscript{5}COOH, H\textsubscript{2}P\textsubscript{3}O\textsubscript{10} and H\textsubscript{2}O. The thermal analysis showed that the compound is stable between 25 and 90°C and has confirmed the number of water molecules per formula unit. This loss of water takes place in one step and leads to the crystallization of the anhydrous phase, (C\textsubscript{6}H\textsubscript{5}NO\textsubscript{2})\textsubscript{2}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}, which was characterized by its X-ray powder diffraction pattern and IR spectrum. This phase (C\textsubscript{6}H\textsubscript{5}NO\textsubscript{2})\textsubscript{2}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10} was found stable in a small temperature range, 150-160°C. We have shown that by raising the temperature, the anhydrous phase

Table 5. Activation energy values Ea, pre-exponential factor (A) and correlation coefficient (r\textsuperscript{2}) calculated by Ozawa and KAS methods for the dehydration of (NH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}COOH)\textsubscript{3}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O under atmospheric pressure.

<table>
<thead>
<tr>
<th>Steps</th>
<th>OZAWA</th>
<th>K.A.S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ea (kJ/mol)</td>
<td>A (min\textsuperscript{-1})</td>
</tr>
<tr>
<td>Step 1 (3H\textsubscript{2}O)</td>
<td>75.6954</td>
<td>2.3714×10\textsuperscript{-12}</td>
</tr>
<tr>
<td>Step 2 (2NH\textsubscript{3})</td>
<td>99.9956</td>
<td>7.8151×10\textsuperscript{-12}</td>
</tr>
<tr>
<td>Step 3 (1NH\textsubscript{3})</td>
<td>112.9685</td>
<td>4.3858×10\textsuperscript{-12}</td>
</tr>
<tr>
<td>Step 4 (3CO\textsubscript{2})</td>
<td>92.9084</td>
<td>3.9084×10\textsuperscript{-12}</td>
</tr>
</tbody>
</table>

Table 6. Values of \(\Delta S\), \(\Delta H\) and \(\Delta G\) for dehydration step of (NH\textsubscript{3}C\textsubscript{6}H\textsubscript{5}COOH)\textsubscript{3}H\textsubscript{2}P\textsubscript{3}O\textsubscript{10}.3H\textsubscript{2}O calculated according to Ozawa and KAS equations.

<table>
<thead>
<tr>
<th>Steps</th>
<th>OZAWA</th>
<th>K.A.S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Delta S) (J.K\textsuperscript{-1}.mol\textsuperscript{-1})</td>
<td>(\Delta H) (kJ.mol\textsuperscript{-1})</td>
</tr>
<tr>
<td>Step 1 (3H\textsubscript{2}O)</td>
<td>-19.2678</td>
<td>72.1619</td>
</tr>
<tr>
<td>Step 2 (2NH\textsubscript{3})</td>
<td>-10.3472</td>
<td>96.0132</td>
</tr>
<tr>
<td>Step 3 (1NH\textsubscript{3})</td>
<td>-15.1501</td>
<td>108.98614</td>
</tr>
<tr>
<td>Step 4 (3CO\textsubscript{2})</td>
<td>-16.5641</td>
<td>91.0571</td>
</tr>
</tbody>
</table>
loses successively $3H_2O$ ((2) $NH_3$, (1) $NH_3$) and $3CO_2$ per formula unit. For each of these entities released, the apparent activation energy was measured. These energies are respectively 73.4 kJ/mol for 1 $NH_3$ and 92.29 kJ/mol for $3CO_2$. Between 260 and 300°C, the residual mass, (C$_6$H$_9$)$_2$H$_2$P$_3$O$_{10}$ undergoes a weight loss corresponding to a molar loss of 70 g/mol. This weight loss is accompanied by an atomic rearrangement which results on the DSC thermogram with a peak at 300°C. Beyond 300°C, there is degradation of the organic matrix and / or the mineral matrix. An exothermic peak at the top temperature at 432°C could be the combustion of the residue of the organic matrix.

References


6- J. Chékir-Mzali, S. Elgharbi, K. Horchani-Naifer, M. Ferid, Synthesis, vibrational characteristic and luminescence properties of $Er^{3+}$ in HNH$_2$ErP$_2$O$_{10}$, Optical Materials, 2017, 37, 188.

7- A. Charaf, I. Fahim, EL. M. Tace, M. Tridane, M. Radid and S. Belaaoud, Physico-chemical studies of CuNa$_3$P$_2$O$_5$·H$_2$O, crystallographic characterization of CuNa$_3$P$_2$O$_5$ and quantum chemical calculations of Th PO$_{10}^{5+}$ ion, Phosphorus Research Bulletin, 2010, 24, 83.


9- I. Fahim, M. Tridane and S. Belaaoud, Physico-chemical studies of MgNa$_3$P$_2$O$_{10}$·12H$_2$O, XIIème Rencontre Marocaine sur la Chimie de l’Etat Solide (REMICES XII), MATEC Web of Conferences, 2013, 5, 04035.

10- M. Tridane, I. Fahim, S. Benmokhtar and S.Belaaoud, Structural modifications from NiNa$_3$P$_2$O$_{10}$·12H$_2$O to NiNa$_3$P$_2$O$_{10}$ new triphosphate during the dehydration process, Phosphorus Research


12- M. Belhabra, S. Zerraf, A. Kheireddine, K. El Kababi, A. atibi, M. tridane, M. Radid, and S. Belaaoud, Chemical preparation and crystallographic characterization of BaCsP$_2$O$_5$·2H$_2$O, (NH$_4$)$_2$H$_2$COOH)·H$_2$P$_2$O$_{10}$·3H$_2$O10 and it is corresponding anhydrous, (NH$_4$)$_2$H$_2$COOH)·H$_2$P$_2$O$_{10}$, Am. J. innov. res. Appl. sci., 2017, 6(4), 223-229.


22- V. Koval, P. Nagornyi, Effect of addition of ammonium dihydrophosphate on the formation of insoluble polyphosphates by condensation of potassium dihydrophosphate at 225°C, J Appl chem., 1990, 62, 2373