Supplementary Information

Disproportionation of hypophosphite and phosphite

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An indication of what happens with the water that does not escape to the gas phase can be obtained from the stoichiometry of the solid and gaseous products. Heating NaH$_2$PO$_2$ leads to the formation of solid sodium phosphites and phosphates and gaseous PH$_3$. Furthermore, gaseous H$_2$O and H$_2$ may be formed; H$_2$O by condensation and H$_2$ by reaction of H$_2$O with phosphite, as we will see in the following. These gases are responsible for the weight decrease observed in the TG (Fig. 1). At the same time, the Na/P ratio of the solid products increased, as the LS $^{31}$P NMR spectra demonstrated (Fig. 4). The changes in the P/Na, O/Na and H/Na ratios indicate how much PH$_3$ and H$_2$O or H$_2$ escape to the gas phase in the decomposition of hypophosphite and phosphite. When hypophosphite and phosphite were heated to high enough temperature (e.g. 400 °C), none of the P(V) products (Na$_3$P$_3$O$_9$, Na$_5$P$_3$O$_{10}$, Na$_4$P$_2$O$_7$, Na$_3$PO$_4$) contained hydrogen, which means that it is removed as PH$_3$, H$_2$O or as H$_2$. This enables us to determine the coefficients a, b, c, d and e in the equation NaH$_2$PO$_2$ $\gamma$ aPH$_3$ + bNaPO$_3$ + cNa$_3$PO$_4$ + dH$_2$ + eH$_2$O from the mass balances for the Na, H, P and O atoms and the formal charge balance on the P atoms. Only two P(V) compounds need to be considered as independent components, e.g. NaPO$_3$ and Na$_3$PO$_4$, because the other two can be written as a combination of these two compounds (e.g. Na$_4$P$_2$O$_7$ = NaPO$_3$ + Na$_3$PO$_4$ and Na$_4$P$_3$O$_{10}$ = Na$_3$PO$_4$ + 2NaPO$_3$). Because sodium atoms do not escape to the gas phase, all Na atoms present in the reactant end up in the P(V) products. When H$_2$O is not a product, also all O atoms of NaH$_2$PO$_2$ must be in the P(V) products and the above equation becomes 5NaH$_2$PO$_2$ $\gamma$ 2PH$_3$ + 2NaPO$_3$ + Na$_3$PO$_4$ + H$_2$ = 2PH$_3$ + Na$_5$P$_3$O$_{10}$ + H$_2$. When H$_2$O is a product, the equation becomes 4NaH$_2$PO$_2$ $\gamma$ 2PH$_3$ + NaPO$_3$ + Na$_3$PO$_4$ + H$_2$O = 2PH$_3$ + Na$_4$P$_2$O$_7$ + H$_2$O. The results of all possible reactions for hypophosphite, phosphite and mixtures, with either H$_2$ or H$_2$O as product, are presented in Table S1. For each reaction the theoretical weight losses due to the formation of PH$_3$, H$_2$O and H$_2$ are presented, as well as the observed values. Furthermore, the Na/P ratios in the solid product are presented.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Na/P Ratio theory</th>
<th>weight loss (%) exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5NaH_2PO_2 \gamma 2PH_3 + 2NaPO_3 + Na_3PO_4 + H_2 = 2PH_3 + Na_5P_3O_{10} + H_2]</td>
<td>[4NaH_2PO_2 \gamma 2PH_3 + NaPO_3 + Na_3PO_4 + H_2O = 2PH_3 + Na_4P_2O_7 + H_2O]</td>
<td></td>
</tr>
</tbody>
</table>
## Pure compounds

1. \(5 \text{NaH}_2\text{PO}_2 \xrightarrow{\text{R1}} 2 \text{PH}_3 + \text{Na}_2\text{P}_3\text{O}_{10} + 2 \text{H}_2\) 
   \(4 \text{NaH}_2\text{PO}_2 \xrightarrow{\text{R2}} 2 \text{PH}_3 + \text{Na}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}\) 
   \[\begin{array}{ccc}
   \text{W-loss} & \text{R1} & \text{R2} \\
   \hline
   & 1.67 & 16.4 & 16.6 \pm 0.5 \\
   \end{array}\]

2. \(2 \text{NaH}_2\text{PO}_3 \xrightarrow{\text{R1}} \text{Na}_2\text{H}_2\text{P}_2\text{O}_5 + \text{H}_2\) 
   \(15 \text{Na}_2\text{H}_2\text{P}_2\text{O}_5 \xrightarrow{\text{R2}} 6 \text{PH}_3 + 3 \text{Na}_2\text{P}_3\text{O}_{10} + 5 \text{Na}_2\text{P}_3\text{O}_9 + 6 \text{H}_2\) 
   \[\begin{array}{ccc}
   \text{W-loss} & \text{R2} & \text{R1} \\
   \hline
   & 1.25 & 7.6 & 7.5 \pm 0.2 \\
   \end{array}\]

3. \(5 \text{Na}_2\text{HPO}_3 \xrightarrow{\text{R1}} \text{PH}_3 + 2 \text{Na}_2\text{PO}_4 + \text{Na}_2\text{P}_2\text{O}_7 + \text{H}_2\) 
   \(5 \text{Na}_2\text{HPO}_3 \xrightarrow{\text{R2}} \text{P} + 2 \text{Na}_2\text{PO}_4 + \text{Na}_2\text{P}_2\text{O}_7 + 2.5 \text{H}_2\) 
   \[\begin{array}{ccc}
   \text{W-loss} & \text{R2} & \text{R1} \\
   \hline
   & 2.5 & 5.7 & 2.5 \pm 0.8 \\
   \end{array}\]

4. \(2 \text{NaH}_2\text{PO}_3 + 2 \text{Na}_2\text{HPO}_3 \xrightarrow{\text{R1}} \text{Na}_2\text{H}_2\text{P}_2\text{O}_5 + 2 \text{Na}_2\text{HPO}_3 + \text{H}_2\text{O}\) 
   \[\begin{array}{ccc}
   \text{W-loss} & \text{R1} & \text{R2} \\
   \hline
   & 1.5 & \text{both reactants react and are oxidized by water} & 50\% \text{ of PH}_3 \text{ decomposes} \\
   \hline
   \end{array}\]

## Mixtures

5. \(2 \text{Na}_2\text{HPO}_3 + 2 \text{NaH}_2\text{PO}_4 \xrightarrow{\text{R1}} 2 \text{Na}_2\text{HPO}_3 + \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}\) 
   \[\begin{array}{ccc}
   \text{W-loss} & \text{R2} & \text{R1} \\
   \hline
   & 2 \text{Na}_2\text{HPO}_3 + \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \xrightarrow{\text{R1}} \text{Na}_2\text{P}_3\text{O}_{10} + \text{NaPO}_3 + 2 \text{H}_2 \\
   \end{array}\]

*both reactants react and are oxidized by water, \(\uparrow\)both reactants react and are oxidized by water, 50\% of PH\(_3\) decomposes, \(\uparrow\)only Na\(_2\)H\(_2\)P\(_2\)O\(_5\) reacts.

### Table S2 Possible mechanisms for the first step of the disproportionation of NaH\(_2\)PO\(_2\)

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>(\uparrow)W-loss</th>
<th>(\text{R1})</th>
<th>(\text{R2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Disproportionation and condensation of NaH(_2)PO(_3)</td>
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</tbody>
</table>
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Several mechanisms can be written in which NaH₂PO₂, Na₂H₂P₂O₅ or Na₂HPO₃ are oxidized by water (Table S2), but not all mechanisms agree with the experimental results. The LS NMR spectra (Fig. 4) show that Na₂H₂P₂O₇ appears immediately at 300 °C, simultaneously with Na₂H₂P₂O₅ and phosphite.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Weight Loss (%)</th>
<th>Na₂H₂P₂O₅ (%)</th>
<th>Na₂HPO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6NaH₂PO₂ $\rightarrow$ 2PH₃ + Na₂H₂P₂O₅ + 2Na₂HPO₃ + H₂O</td>
<td>16.3</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4NaH₂PO₂ $\rightarrow$ PH₃ + Na₂H₂P₂O₅ + Na₂HPO₃ + H₂</td>
<td>12.3</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>20NaH₂PO₂ $\rightarrow$ 6PH₃ + 3Na₂H₂P₂O₅ + 6Na₂HPO₃ + Na₂H₂P₂O₇ + 4H₂</td>
<td>12.0</td>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td>10NaH₂PO₂ $\rightarrow$ 3PH₃ + 2Na₂H₂P₂O₅ + Na₂HPO₃ + Na₂P₂O₇ + 3H₂</td>
<td>12.3</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td>14NaH₂PO₂ $\rightarrow$ 4PH₃ + 3Na₂H₂P₂O₅ + 3Na₂HPO₃ + Na₂HPO₄ + 3H₂</td>
<td>11.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>12NaH₂PO₂ $\rightarrow$ 4PH₃ + Na₂H₂P₂O₅ + Na₂H₂P₂O₇ + 4Na₂HPO₃ + 2H₂</td>
<td>13.3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>12NaH₂PO₂ $\rightarrow$ 4PH₃ + 2Na₂H₂P₂O₅ + 2Na₄P₂O₇ + 4H₂</td>
<td>13.6</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>24NaH₂PO₂ $\rightarrow$ 8PH₃ + 3Na₂H₂P₂O₅ + 6Na₂HPO₃ + Na₂H₂P₂O₇ + 2Na₂HPO₄ + 4H₂</td>
<td>13.3</td>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td>18NaH₂PO₂ $\rightarrow$ 6PH₃ + 3Na₂H₂P₂O₅ + 2Na₂HPO₃ + 2Na₂HPO₄ + Na₄P₂O₇ + H₂</td>
<td>13.4</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>10. 1. and oxidation of Na₂HPO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12NaH₂PO₂ $\rightarrow$ 4PH₃ + 2Na₂H₂P₂O₅ + 2Na₂HPO₃ + 2Na₂HPO₄ + 2H₂</td>
<td>13.3</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

*Weight loss by PH₃, H₂O and H₂ (%), *Na₂HPO₃/2(Na₂H₂P₂O₅), *(Na₂H₂P₂O₇+Na₄P₂O₇)/Na₂H₂P₂O₅
as if it is a primary product. Therefore, only mechanisms in which water oxidizes hypophosphite or pyrophosphite to pyrophosphate need to be considered. Mechanisms in which Na₂HPO₃ is oxidized to Na₂HPO₄ can be omitted, because Na₂HPO₄ does not condense to Na₄P₂O₇ below 370 °C. This means that mechanisms 1, 2, 5 and 10 of Table S1 can be disregarded. Furthermore, already at the start of the reaction at 300 °C the intensity of the phosphite NMR peak at 3.25 ppm is smaller than that of the pyrophosphate peak at -4.99 ppm (Fig. 4). This means that less Na₂HPO₃ is formed than Na₂H₂P₂O₅ (Fig. 4), meaning that mechanisms 3, 6 and 8 can be disregarded as well. Mechanism 7 cannot explain the results either, because it does not predict any formation of Na₂HPO₃. At higher temperature (310-360 °C) the intensity of the phosphite NMR peak, and thus the concentration of Na₂HPO₃, decreases strongly. This indicates that, once formed, Na₂HPO₃ reacts to Na₂HPO₄ by oxidation by water (H₂O + Na₂HPO₃ $\rightarrow$ H₂ + Na₂HPO₄) or to NaH₂PO₃ by H-Na exchange (2Na₂HPO₃ + Na₂H₂P₂O₇ $\rightarrow$ 2NaH₂PO₃ + Na₄P₂O₇). The exchange transforms Na₂HPO₃, which itself does not react below 450 °C, into reactive NaH₂PO₃. The required Na₂H₂P₂O₇ can be formed by oxidation of NaH₂PO₂ and Na₂H₂P₂O₅ by water.

![Fig. S1](image_url)  
**Fig. S1**  TG-DSC curves of NaH₂PO₂·H₂O in N₂.
Fig. S2       TG-DTG curves of NaH$_2$PO$_2$·H$_2$O in 10% H$_2$ in N$_2$ (v/v).

Fig. S3       XRD patterns of the products of heating NaH$_2$PO$_2$ in H$_2$ to different temperatures.
Fig. S4  XRD pattern of the product of heating Na$_2$HPO$_2$ at 360 °C in N$_2$ for 1 h.

Fig. S5  Solutions and suspensions of 30 mg of the solids obtained after heating NaH$_2$PO$_2$ in N$_2$ to 260, 280, 300, 330, 360 and 400 °C (from left to right) dissolved in D$_2$O, after shaking (left) and after settling for two days (right).
Fig. S6  Normal $^{31}$P NMR spectra of solutions of the products of heating NaH$_2$PO$_2$·H$_2$O in N$_2$ to 280, 300, 330, 360 and 400°C.

Fig. S7  Expansion of the normal $^{31}$P NMR spectrum of the product of heating NaH$_2$PO$_2$·H$_2$O in N$_2$ to 330 °C.
Fig. S8  TG-DTG (left) and TG-DSC (right) curves of NaH$_2$PO$_3$·H$_2$O in N$_2$.

Fig. S9  XRD patterns of the products of heating NaH$_2$PO$_3$ in N$_2$ to 280, 360 and 400 °C.
Fig. S10 Normal $^{31}$P NMR spectrum of the product of heating NaH$_2$PO$_3$ in N$_2$ to 280, 360 and 400 °C.

Fig. S11 TG-DTG (left) and TG-DSC (right) curves of Na$_2$HPO$_3$·5H$_2$O in N$_2$. 
Fig. S12  XRD patterns of the products of heating Na$_2$HPO$_3$ in N$_2$ at 360 and 500 °C for 1 h.

Fig. S13  The proton-decoupled $^{31}$P LS-NMR of the products of heating Na$_2$HPO$_3$ in N$_2$ to 360 and 500 °C.
Fig. S14 The solutions and suspensions of the products of heating NaH$_2$PO$_3$ to 280, 360 and 400 °C (the first three from left to right); heating Na$_2$HPO$_3$ to 360 and 500 °C (4th-5th); NaHPO$_3$ + NaH$_2$PO$_3$ (1:1) to 360 and 400 °C (6th-7th); Na$_2$HPO$_3$ + NaH$_2$PO$_4$ (1:1) 360 and 400 °C (8th-9th); Na$_2$HPO$_3$ + Na$_2$HPO$_4$ (1:1) to 400 °C (10th) (all samples were heated in N$_2$).

Fig. S15 TG-DTG (left) and TG-DSC (right) of a 1:1 mixture of NaH$_2$PO$_3$H$_2$O and Na$_2$HPO$_3$5H$_2$O in N$_2$. 
**Fig. S16**  XRD patterns of the products of heating a 1:1 mixture of Na$_2$HPO$_3$ and NaH$_2$PO$_3$ in N$_2$ to 280, 360 and 400 °C.

**Fig. S17**  Normal $^{31}$P NMR spectrum of the solution of the product of heating a 1:1 mixture of Na$_2$HPO$_3$ and NaH$_2$PO$_3$ in N$_2$ to 400 °C after adding one drop concentrated HCl (before adding HCl, pH=9; after addition, pH=1).
**Fig. S18**  Raman spectrum of the product of heating Na$_2$HPO$_3$+NaH$_2$PO$_3$ (1:1) in N$_2$ to 360 °C.

**Fig. S19**  TG-DSC curves of Na$_2$HPO$_3$·5H$_2$O +NaH$_2$PO$_4$·2H$_2$O (1:1) in N$_2$. 
Fig. S20  XRD pattern of the products of heating Na$_2$HPO$_3$ + NaH$_2$PO$_4$ (1:1) in N$_2$ to 360 °C.

Fig. S21 TG-DSC curves of NaH$_2$PO$_4$·2H$_2$O in N$_2$.

The predicted reactions and weight changes are

at 150 °C:  \[ \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{NaH}_2\text{PO}_4 + 2\text{H}_2\text{O} \quad \Delta = 100\times36/156 = 23.1\% \]
at 220 °C: $2\text{NaH}_2\text{PO}_4 \xrightarrow{\Delta} \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$  
$\Delta = 100 \times \frac{18}{2} \times 156 = 5.8\%$

at 320 °C: $3\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \xrightarrow{\Delta} 2\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10} + \text{H}_2\text{O}$  
$\Delta = 100 \times \frac{18}{6} \times 156 = 1.9\%$

at 360 °C: $2\text{Na}_3\text{H}_2\text{P}_3\text{O}_{10} \xrightarrow{\Delta} 2\text{Na}_3\text{P}_3\text{O}_9 + 2\text{H}_2\text{O}$  
$\Delta = 100 \times \frac{36}{6} \times 156 = 3.8\%$

Fig. S22  
TG-DSC curves of Na$_2$HPO$_4$·12H$_2$O in N$_2$.

The predicted reactions and weight changes are

at 120 °C: Na$_2$HPO$_4$·12H$_2$O $\xrightarrow{\Delta}$ Na$_2$HPO$_4$ + 12H$_2$O  
$\Delta = 100 \times \frac{216}{358} = 60.3\%$

at 350 °C: 2Na$_2$HPO$_4$ $\xrightarrow{\Delta}$ Na$_4$P$_2$O$_7$ + H$_2$O  
$\Delta = 100 \times \frac{18}{2} \times 358 = 2.5\%$