UDC 546.185.712:543.226

Thermal properties of $Mn(H_2PO_4)_2 \cdot 4H_2O$ and products of his dehydration

N.M. Antraptseva, N.V. Solod
National university of Life and Environmental Sciences of Ukraine

Hydrated dihydrogenphosphates of manganese(II) and products of their dehydration are widely used as the basis of various inorganic materials: catalysts of organic synthesis, thermophosphoric decorative coatings, corrosion inhibitors and others. Thermal properties of manganese(II) dihydrogenphosphate tetrahydrate - $Mn(H_2PO_4)_2 \cdot 4H_2O$ was discussed in literature, superficially, in the context of research of its structure. The purpose of the present work - to investigate thermal properties of $Mn(H_2PO_4)_2 \cdot 4H_2O$, composition, temperature intervals of formation and thermal stability of products of its partial and complete dehydration, to set the sequence of thermal solidphase transformations.

In accordance with the results of differential thermal analysis, $Mn(H_2PO_4)_2 \cdot 4H_2O$ proof at heating on air with speed a 2.5 °/min to 50°C. The further increase of temperature is accompanied by the loss of mass, that on the thermogravymetric curve (TG) registers four quite distinct stages in the intervals of 50-110°C (3 maximums at 60, 80 and 100°C), 110-160°C (maximum at 120°C), 160-220°C (maximum at 180°C) and 275-335°C (2 maximums at 295 and 310°C).

The results of complex analysis of products of partial dehydration showed that practically simultaneously with beginning of dehydration except the solid phase, registers the liquid - free phosphate acid amount of which during the removal of 1.66 mole H_2O at 105°C is 1.21% (in a count on P_2O_5). The main component of multiphase product of dehydration of $Mn(H_2PO_4)_2 \cdot 4H_2O$ on the first stage is dihydrate - $Mn(H_2PO_4)_2 \cdot 2H_2O$, identified according to X-ray and IR spectroscopic analysis. The second product is less protonated phosphate of composition $MnHPO_4 \cdot 3H_2O$. Interpretation of the obtained data shows that the heat treatment of $Mn(H_2PO_4)_2 \cdot 4H_2O$ in the range of 50 - 110°C is accompanied by removal after the molecular mechanism of two least strongly adhesive in its structure crystallizational water molecules. However, accordingly to the TG curve, their complete removing is not happening (the losses of mass is 1.7 mole H_2O only). This indicates that the free phosphoric acid, which is formed, dissolved in water, preventing its removal.

The same for the chemistry process proceeds on the second stage of dehydration of initial tetrahydrate. Its ends with formation in an interval 110 - 160°C mixture of two crystalline phases, the main of which is anhydrous dihydrogenphosphate $Mn(H_2PO_4)_2$. The second phase is a phosphate of composition $Mn_5(HPO_4)_2(PO_4)_2 \cdot 4H_2O$ - product of disproportionation of hydrogenphosphate on a scheme: $5MnHPO_4 \cdot 3H_2O \rightarrow Mn_5(HPO_4)_2(PO_4)_2 \cdot 4H_2O + H_3PO_4 + 11H_2O$.

As a result the amount of free H_3PO_4 in partial thermolysis products of $Mn(H_2PO_4)_2 \cdot 4H_2O$ increases and at 160°C is 2.12 % P_2O_5. One of the sources of its formation on the second stage of dehydration of initial tetrahydrate, in addition, there is a process of intramolecular hydrolysis of $Mn(H_2PO_4)_2 \cdot 2H_2O$.

On the third stage of thermolysis of $Mn(H_2PO_4)_2 \cdot 4H_2O$ the process of anionic condensation begins actively. At 185°C, when the losses of mass answer removing of 4.55 mole H_2O, in composition of salt component the condensed phosphates formed with $n = 2 \div 5$, in composition of acid - polyphosphate acids of general formula

$H_{n+2}P_nO_{3n+1}$, where n = 2 ÷ 4. At heating of $Mn(H_2PO_4)_2 \cdot 4H_2O$ to 275°C it is presented by mixture of X-ray amorphous high molecular oligohosphates, the amount of phosphorus atoms in the chain of which varies from 3 to 8 and more, and polyphosphate acids with $2 \leq n \leq 7$. The total content of P_2O_5 in a salt component increases to 53,4 mas.%, in acid - reduced to 11 mas.%, characterizing cooperations that will be realized between them. The degree of transformation of monophosphatic anion in a salt component arrives at 94,6 %, in acidic - 84,5 %.

Further heating of $Mn(H_2PO_4)_2 \cdot 4H_2O$ to 300°C is accompanied by simplification of anionic composition of thermolysis products and reduction to the amount of polyphosphate acids, specifying on their direct participating in formation of new phosphate with the circular structure of anion. About beginning of crystallization of finish thermolysis products, identified as cyclo-tetraphosphate of composition $Mn_2P_4O_{12}$, shows exothermic effect with a maximum at 295°C. Forming of crystalline structure of cyclo-tetraphosphate is completed at 335°C - to the temperature practically complete dehydration of initial tetrahydrate. $Mn_2P_4O_{12}$ is crystallizable in monoclinic system (sp. gr. C2/c, Z = 4) with unit cell parameters, nm; a = 1.2084, b = 0.8471, c = 1.0171; $\beta = 119.29^o$.

Thus, dehydration of $Mn(H_2PO_4)_2 \cdot 4H_2O$ occurs simultaneously in two directions with formation of cyclo-tetraphosphate of $Mn_2P_4O_{12}$. First - envisages thermal dehydration of the protonated condensed phosphates (to 65 %). Accordance with the second direction, to 35% $Mn_2P_4O_{12}$ formed as a result of solidphase cooperation of partial dehydration products (polyphosphate acids and middle oligohosphates).