Thermochimica Acta, 88 (1985) 415–419
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PROBLEMS CONNECTED WITH THE MELTING OF Ni^{II}, Co^{II} AND Mn^{II} CYCLO-TETRAPHOSPHATES

M. TROJAN and D. BRANDOVÁ

Institute of Chemical Technology, 532 10 Pardubice (Czechoslovakia)

(Received 27 December 1984)

ABSTRACT

Differential thermal analysis has been used to follow the process of melting of Ni^{II}, Co^{II} and Mn^{II} cyclo-tetraphosphates. The melting is congruent in a dry atmosphere, being non-congruent in the presence of small amounts of water vapour: the tetraphosphate cycles are split and further condensed to chains of higher linear phosphates. Their end groups (and hence their stability) are provided by water molecules present in the atmosphere. After cooling the products have a glassy amorphous form. By repeated heating they are changed back into the cyclo-tetraphosphates with crystalline character, and the water molecules are released.

INTRODUCTION

The available literature data on melting of the cyclo-tetraphosphates investigated are incomplete and non-uniform. Some authors [1,2] do not consider any changes during the melting process. Others [3] mention unequivocally only the congruency, and still others [4–6], on the contrary, only the non-congruency. Also, the melting temperatures given for the substances studied are non-uniform. Some authors [4] even mention possible incomplete recrystallization of the amorphous products of the non-congruent melting of the cyclo-tetraphosphates, except for the cobalt(II) product, without any data about the conditions of these processes. In our previous papers [7–9] we used thermal analyses to follow the reactions of formation of Mn^{II} and Co^{II} cyclo-tetraphosphates. These studies showed that the compounds melted in two ways. Either in a congruent way, or with splitting of the tetraphosphate cycles into chains with subsequent condensation. An explanation was suggested [9] that the melting characteristics of the cyclo-tetraphosphates could be connected with the presence of water vapour in the atmosphere, provided the sample carrier is absolutely inert (to the phosphate melt). Therefore, DTA was carried out on the Mn^{II}, Co^{II} and Ni^{II} cyclo-tetraphosphates with a VDTA 8 M2 apparatus (system "Kiev") enabling measurements in a precisely defined atmosphere.

0040-6031/85/$03.30

METHODS

The pure Ni^{II}, Co^{II} and Mn^{II} cyclo-tetraphosphates were prepared in our laboratory [7–9]. The DTA measurements were carried out by means of a high-temperature differential thermal analyzer (VDTA 8 M2, system "Kiev") constructed by the Pilot Design Bureau of the Institute of Metal Physics of the Academy of Sciences of the Ukrainian SSR. The sample and standard carriers are placed in the apparatus in a tempered tungsten block and closed in an evacuated chamber. Therefore, the DTA can be measured in vacuum or in a precisely defined inert atmosphere. The arrangement of the apparatus enables extensive regulation of heating and cooling (the rate of temperature increase or decrease used was 40°C min^{-1}) with simultaneous high sensitivity (W/W–20% Re thermocouples of the string type). The investigation of the influence of atmosphere (water vapour) on the melting characteristics of the cyclo-tetraphosphates necessitated application of sample carriers made of materials completely inert to the aggressive phosphate melt. Out of the materials tested (alumina, beryllium(II) oxide, platinum, molybdenum), molybdenum proved to be the most suitable. The apparatus was calibrated (i.e., its temperature axis was determined) with the use of potassium sulphate, potassium chromate, metallic aluminium, copper and iron. The calibration was carried out for both types of atmosphere used in the measurements, i.e., helium atmosphere (0.1 MPa) and vacuum (10 mPa) (the chamber was always repeatedly rinsed with helium). To attain the necessary presence of water vapour in the helium atmosphere, a third crucible was placed on the cover of the tempered tungsten block in the measuring chamber. This crucible contained 100 mg of cobalt(II) dihydrogenphosphate dihydrate. About 2 mg of water vapour per 1 l of the helium atmosphere was released from this substance during the tempering.

To reveal possible weight changes during calcination of the cyclo-tetraphosphates, these substrates were also submitted to thermogravimetry with a Paulik–Paulik–Erdey MOM derivatograph (Q-1500).

The samples from DTA were analyzed by instrumental analytical methods (TLC, X-ray diffraction analysis, IR spectroscopy, NMR).

RESULTS AND DISCUSSION

The DTA curves of the Ni^{II}, Co^{II} and Mn^{II} cyclo-tetraphosphates measured in vacuum (10 mPa) are given in Fig. 1. At the heating rate used (40°C min^{-1}) the melting is associated with distinct endothermic effects in the case of c-$Ni_2P_4O_{12}$ at 1250°C, c-$Co_2P_4O_{12}$ at 1060°C, and c-$Mn_2P_4O_{12}$ at 950°C. The corresponding DTA curves on cooling showed the respective exothermic effects of solidification. The melting and solidification effects of each sample were recorded several times during repeated heating and cooling cycles,

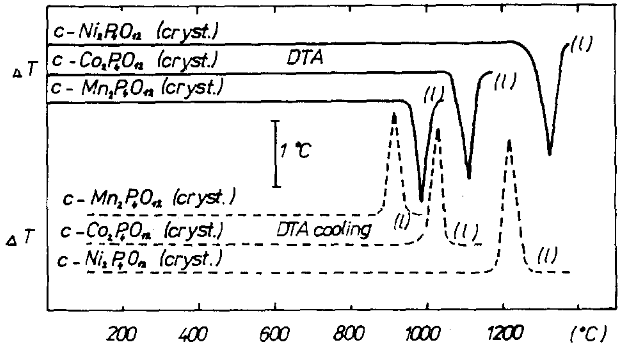

Fig. 1. The DTA curves of c-$Ni_2P_4O_{12}$, c-$Co_2P_4O_{12}$ and c-$Mn_2P_4O_{12}$ in vacuum (10 mPa)—VDTA 8 M2 apparatus (system "Kiev"), heating (cooling) rate, 40°C min^{-1}; sample weight, 100 mg; standard α-Al_2O_3; Mo crucible with a lid.

always being observed at the same temperatures and to the same extent. The instrumental analytical methods confirmed that the solidified samples, even after repeated remelting in vacuum, only contained microcrystals of the individual cyclo-tetraphosphates. Hence, under these conditions the melting of Ni^{II}, Co^{II} and Mn^{II} is congruent.

The DTA curves of the cyclo-tetraphosphates measured in a helium atmosphere (0.1 MPa) containing small amounts of water vapour (2 mg H_2O per l) are given in Fig. 2A. Again the melting takes place at the same temperatures as for that carried out in vacuum, the endothermic effects being, however, somewhat greater. The cooled samples were glassy products. The DTA curves showed no effects corresponding to solidification of the melt (which is a frequent phenomenon with glasses). The instrumental analytical methods confirmed their composition: molecules of higher linear condensed phosphates with non-crystalline amorphous character. It is only the water molecules present in the helium atmosphere which can provide end groups for these linear chains and stabilize them. Generally, the formula $[Me(PO_3)_2]_n \cdot H_2O$ (Me = Ni, Co, Mn) can be suggested for these glassy products. Their repeated heating is connected with relatively distinct exothermic effects at 880 (Ni), 800 (Co) and 770°C (Mn). The instrumental analytical methods showed that these effects correspond to crystallization of the glassy products with restoration of the cyclo-tetraphosphate molecules. This process should be accompanied by release of the water molecules. If the glassy products were ground before the repeated heating, the recrystallization took place at temperatures 200–250°C lower (– · –, Fig. 2), and water was released more easily. Further heating of the cyclo-tetraphosphates formed by recrystallization of the glasses results in their melting at the same temperatures as the starting phosphates. In the helium atmosphere containing water vapour this occurs again with formation of the glassy, higher linear condensed phosphates. Hence, the transition of cyclo-tetraphosphates to these glassy product represents a reversible process.

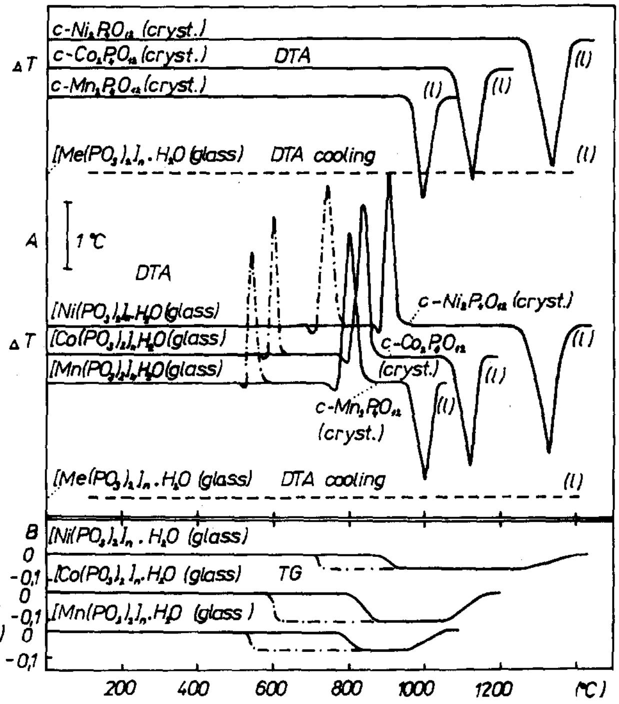

Fig. 2. (A) DTA curves of c-$Ni_2P_4O_{12}$, c-$Co_2P_4O_{12}$ and c-$Mn_2P_4O_{12}$ in a helium atmosphere (0.1 MPa) containing 2 mg H_2O per 1 He. VDTA 8 M2 apparatus (system "Kiev"); heating (cooling) rate, 40°C min^{-1}; sample weight, 100 mg; standard α-Al_2O_3; Mo crucible (opened). (B) TG curves of $[Ni(PO_3)_2]_n \cdot H_2O$, $[Co(PO_3)_2]_n \cdot H_2O$ and $[Mn(PO_3)_2]_n \cdot H_2O$ in a wet argon atmosphere. Derivatograph, Q-1500 apparatus; heating rate, 20°C min^{-1}; sample weight, 1000 mg; standard α-Al_2O_3; Pt crucible (opened); sensitivity of the TG balance, 20 mg.

The participation of water in the processes mentioned, which could be detected by weight changes, was followed thermogravimetrically (Fig. 2B). The measurements were carried out at high sensitivity of TG in humid argon atmosphere. It was found that the recrystallization, i.e., transformation of the glassy products into the cyclo-tetraphosphates, is accompanied by a weight decrease (0.06–0.11%). On the other hand, in the temperature regions of melting of the cyclotetraphosphates a comparable weight increase of the sample occurs (a similar effect is also given [9] for trisodium cyclo-tetraphosphate). The weight changes of the thermoanalyzed samples corresponding to binding (or release) of water molecules were used for calculation of the n value in the glass formulae $[Me(PO_3)_2]_n \cdot H_2O$. These values varied within the limits 35–40, 40–45 and 65–70 for the Co, Mn and Ni glasses, respectively. The n values will obviously be affected by the amount of water vapour in the atmosphere during formation of these glassy products. With respect to the slight weight changes connected with the processes investigated and to the sensitivity of the apparatus used, they must only be considered as orientation values. So far no instrumental analytical method exists which could measure these data with more precision.

CONCLUSION

The melting of the cyclo-tetraphosphates examined is congruent in a dry atmosphere. In the presence of a small amount of water vapour, the tetraphosphate cycles are split at the melting temperature, and the chains formed are condensed to form higher linear phosphates. The chains, composed of several tens of $-PO_3-$ groups, end with the participation of water molecules. Reheating of the glassy products results in their crystallization with release of the water molecules and regeneration of cyclo-tetraphosphate molecules. The reversible process can be represented as follows:

$$1/2\text{c-}Me_2P_4O_{12}\,(\text{cryst.}) \xrightarrow[1/nH_2O]{T_{\text{melting}}} 1/n\,[Me(PO_3)_2]_n \cdot H_2O_{(l)}$$

$$\xrightarrow[(\text{cooling})]{T_{\text{melting}}-25^{\circ}C} 1/n\,[Me(PO_3)_2]_n \cdot H_2O(\text{glass}) \xrightarrow[-1/nH_2O]{T_{\text{cryst.}}(\text{heating})} 1/2\text{c-}Me_2P_4O_{12}\,(\text{cryst.})$$

T_{melting} for $Ni^{II} = 1250$; $Co^{II} = 1060$; $Mn^{II} = 950°C$. $T_{\text{cryst.}}$ for $Ni^{II} = 880$ (770); $Co^{II} = 800$ (580); $Mn^{II} = 770°C$ (530°C); values in parentheses are for ground samples.

REFERENCES

1 J.F. Sarver, Trans. Br. Ceram. Soc., 65 (1966) 191.
2 A.P. Dindune and Z.A. Konstant, Izv. Akad. Nauk Litv. SSR, Ser. Khim., (1974) 111.
3 B.V. Martynenko and M.V. Goloschapov, Izv. Akad. Nauk SSSR, Neorg. Mater., 7 (1971) 1200.
4 E. Thilo and H. Grunze, Z. Anorg. Allg. Chem., 290 (1957) 209.
5 A.I. Dimante, J.G. Kljava, Z.A. Konstant and J.J. Pupans, Zh. Neorg. Khim., 21 (1976) 627.
6 Z.A. Konstant and A.I. Dimante, Izv. Akad. Nauk SSSR, Neorg. Mater., 13 (1977) 99.
7 M. Trojan, D. Brandová and Z. Šolc, Thermochim. Acta, 85 (1985) 99.
8 D. Brandová and M. Trojan, J. Therm. Anal., 30 (1985) 157.
9 M. Trojan, J.D. Seropegin and D. Brandová, Sb. Ved. Pr. Vys. Sk. Chemickotechnol., Pardubice, 47 (1985) 25.