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KINETICS OF SODIUM CYCLOTRIPHOSPHATE HEXAHYDRATE DEHYDRATION

V.M. GALOGAŽA, E.A. PRODAN, S.I. PYTLEV and I. RISTIĆ

University of Belgrade, Faculty of Technology and Metallurgy, 11 000 Belgrade (Yugoslavia) and Institute of General and Inorganic Chemistry of the Academy of Sciences of the B.S.S.R., 220606 Minsk (U.S.S.R.)

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ABSTRACT

Thermogravimetry (TG) and electron microscopy (EM) methods were used to study the isothermal dehydration of $Na_3P_3O_9 \cdot 6H_2O$ single crystals and polycrystalline samples in flowing nitrogen at 35–60°C. The effect of granulometry on the kinetic characteristics of reversible dehydration, which under conditions of uniform localization proceeds with an induction period, self-acceleration and deceleration, was studied.

INTRODUCTION

The results of investigating dehydration at the surface [1,2] and within the volume [3] of $Na_3P_3O_9 \cdot 6H_2O$ single crystals indicate that the flat or undulating dehydration front advances along the surface and into the volume of the crystals without causing their fragmentation. The porous product forming during this process has a comparatively high gas permeability due to rapid $Na_3P_3O_9$ crystallization. Thickening of this layer does not lead to diffusion deceleration of the reaction, which in the stage of removal of the main part of crystal water proceeds in the kinetic region according to the scheme

$$Na_3P_3O_9 \cdot 6H_2O(\text{cryst.}) \rightarrow Na_3P_3O_9(\text{cryst.}) + 6H_2O\uparrow$$

$Na_3P_3O_9$ crystallization, according to X-ray phase studies, is almost simultaneous with the destruction of the initial lattice.

This paper is aimed at determining the kinetic characteristics of dehydration of $Na_3P_3O_9 \cdot 6H_2O$ polycrystalline samples and comparing the results obtained with analogous data for single crystals. The experiments were conducted under conditions allowing the realization of a comparatively simple dehydration model, i.e., uniform localization of the process on crystal faces without the formation of isolated reaction nuclei.

EXPERIMENTAL

A polycrystalline sample (crystal size, $D = 0.5$–2.0 mm) of chromatographically pure sodium hexahydrate cyclotriphosphate was obtained

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according to a known method [1]. Its XRD characteristics corresponded to published data for $Na_3P_3O_9 \cdot 6H_2O$ [4]. Single crystals without any visible defects or cut faults were selected. Mild grinding was employed to produce fine crystals with $D = 0.05–0.1$ mm and short grinding in an agate mortar was used to produce a powder-like sample with $D = 0.01–0.02$ mm. All the samples were kept in hermetically sealed ampoules with minimal free volume.

Isothermal dehydration was carried out in a flow of pre-dried nitrogen containing up to 20–30 ppm of water vapour, 7 ppm of oxygen and 2–3 ppm of argon (N_2 feeding rate, 14 ml min^{-1}). Kinetic experiments were conducted using a Perkin-Elmer thermal analysis Lab 1 with a TGS-2 unit, Model FDC-1. The sample (2–11 mg) was placed in a standard Perkin-Elmer Pt-pan, the temperature brought to the necessary values at HR = 160 K min^{-1} and kept constant within $\mp 0.1°C$. DSC experiments were conducted using the same equipment with a Scan Auto Zero DSC-2 unit (N_2 feeding rate, 37 ml min^{-1}; HR = 5–10 K min^{-1}; standard Al-pan). The earlier stages of uniform localization were studied by the carbon replica method using a Philips E.M. 300 electron microscope.

RESULTS AND DISCUSSION

Taking into account the high sensitivity of the $Na_3P_3O_9 \cdot 6H_2O$ dehydration rate to the surrounding atmosphere it is important, while working with polycrystalline samples, to create conditions for unhindered removal of water vapour, not only through the layer of the solid reaction product, but also from internal layers of the powder-like sample to its external geometrical surface and then into the flow of inert gas medium. If such conditions are not realised, the rate of external diffusion exchange becomes the limiting factor of the overall process. This is the reason why DSC experiments do not give satisfactory results with the method of encapsulating the sample into an aluminium capsule. In this case a split in the endothermal effect is reported due to the fact that in a water vapour atmosphere the dehydration of $Na_3P_3O_9 \cdot 6H_2O$ proceeds via formation of intermediate crystal hydrates. Analogous splitting has been observed on covering a single crystal or a polycrystalline sample in the standard pan with an aluminium disc (Fig. 1). Due to this phenomenon DSC experiments, as well as isothermal TG experiments, were carried out using open standard pans with fine crystalline or powder-like samples arranged in a thin layer. Under such conditions only one DSC effect of crystal water removal from $Na_3P_3O_9 \cdot 6H_2O$ is fixed.

The kinetic curves of isothermal dehydration obtained under the above conditions have a peculiar S-form (Fig. 2), which is characteristic of kinetic curves of $Na_3P_3O_9 \cdot 6H_2O$ dehydration under kinetic conditions in vacuum. These curves consist of three main parts: the induction period, self-acceleration, and deceleration. The above facts do not allow us to conclude that

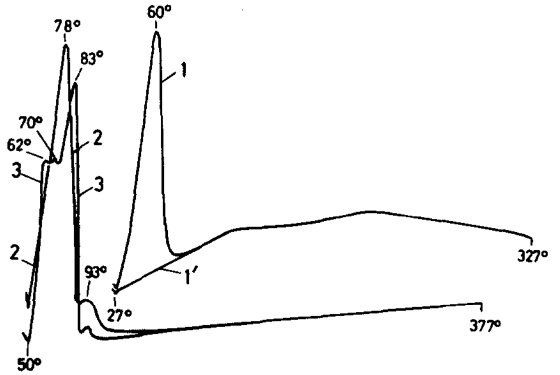

Fig. 1. DSC curves of heating $Na_3P_3O_9 \cdot 6H_2O$ in a flow of nitrogen: (1) sample with $D = 0.05–0.1$ mm, $m = 4.5$ mg, HR = 5 K min^{-1}, open Al-pan; (1′) baseline; (2) crystal, $m = 2.84$ mg, HR = 10 K min^{-1}, Al-pan covered with an Al-disc; (3) sample with $D = 0.01–0.02$ mm, $m = 6.92$ mg, HR = 10 K min^{-1}, Al-pan covered with an Al-disc.

removal of the gaseous reaction products in flowing nitrogen is carried out under the same favourable conditions as in vacuum. Due to the effect of the protective gas jacket, a low partial water vapour pressure is created over the substance. This pressure affects the most sensitive kinetic characteristics of the reaction. For instance, it leads to a decrease in dehydration rate, as

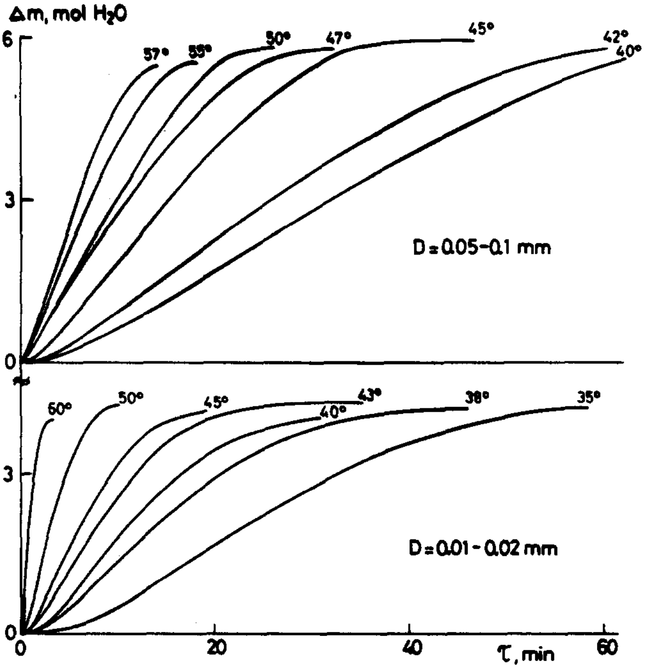

Fig. 2. Dehydration kinetic curves of fine crystalline ($D = 0.05–0.1$ mm) and powder-like ($D = 0.01–0.02$ mm) samples of $Na_3P_3O_9 \cdot 6H_2O$ in a flow of nitrogen.

compared with that in vacuum and, in accordance with the rules of reversible topochemical reactions, it leads to an increase in the effective activation energy, E.

Dehydration of single crystals and of the $Na_3P_3O_9 \cdot 6H_2O$ fine crystalline sample in vacuum is characterized by the effective activation energy, E, of 40–41 kJ mol^{-1}. In the present case the effective activation energy, calculated from the temperature dependence, $1/\tau_{0.5}$ or $1/\tau_{0.25}$ ($\tau_{0.5}$ = half dehydration time, $\tau_{0.25}$ = time of attainment of $\Delta m = 1.5$ mol H_2O), is characterized by higher values: $E = 92$ kJ mol^{-1} ($D = 0.05$–0.10 mm) and $E = 97$ kJ mol^{-1} ($D = 0.01$–0.02 mm). These values are close to $E = 101$ kJ mol^{-1}, which corresponds to the dehydration of $Na_3P_3O_9 \cdot 6H_2O$ in air at relative humidity, $r = 26\%$, and to those previously obtained [3] at the same r value: $E^{\mathrm{v}}_{[100]} = E^{\mathrm{v}}_{[001]} = E^{\mathrm{v}}_{[010]} = 102 \pm 12$ kJ mol^{-1} for single crystals, $E^{\mathrm{v}}_{[100]}$, $E^{\mathrm{v}}_{[001]}$ and $E^{\mathrm{v}}_{[010]}$ being the values of the effective activation energy calculated from the temperature dependence of the linear rate of advancement of the dehydration front from faces (100), (001) and (010) in the volume of the $Na_3P_3O_9 \cdot 6H_2O$ crystal in directions [100], [001], [010], respectively.

The results obtained allow us to suggest that during dehydration in flowing nitrogen the partial pressure of water vapour over the substance does not exceed $r = 26\%$. At the start of reaction the pressure is low, reaching a maximum value as the reaction rate passes through its maximum. Microscopic data show that in flowing nitrogen the localization form of the process is the same as for $r = 0\%$; i.e., uniform localization at low Δm, with the respective crystal faces reacting at the end of the corresponding induction periods.

Uniform localization at low Δm occurs because of comparatively rapid covering of the crystal faces by a large number of non-transparent spots. Among these it is possible to find regularly shaped spots, e.g., parallelograms that are characteristic of face (001) when the crystal is oriented as in ref. 4 (Fig. 3). This form corresponds to a geometrical figure that could be obtained on the basis of structural data [5]. If the structure is projected on face (001) and the straight lines drawn through water molecule layers interconnected with the spacings of one or two elementary cells, a parallelogram with sides parallel to [100] and [010] is obtained.

Experimentally observed parallelogram-like spots grow to large sizes with dehydration under mild conditions ($25\% < r < 50\%$), where the reaction is nucleated on a small number of active centres. In the present case, since the reaction commences under severe conditions and is nucleated on a large number of the centres, the spots do not grow large in size and are sometimes characterized by an irregular form.

The comparatively weak self-acceleration observed during $Na_3P_3O_9 \cdot 6H_2O$ single crystal dehydration (Fig. 4) is explained not by spot-like broadening of the reaction zone, but by the crystal faces starting to react in the order of decreasing activity: first (100), then (001) and (010). On dehydration of the

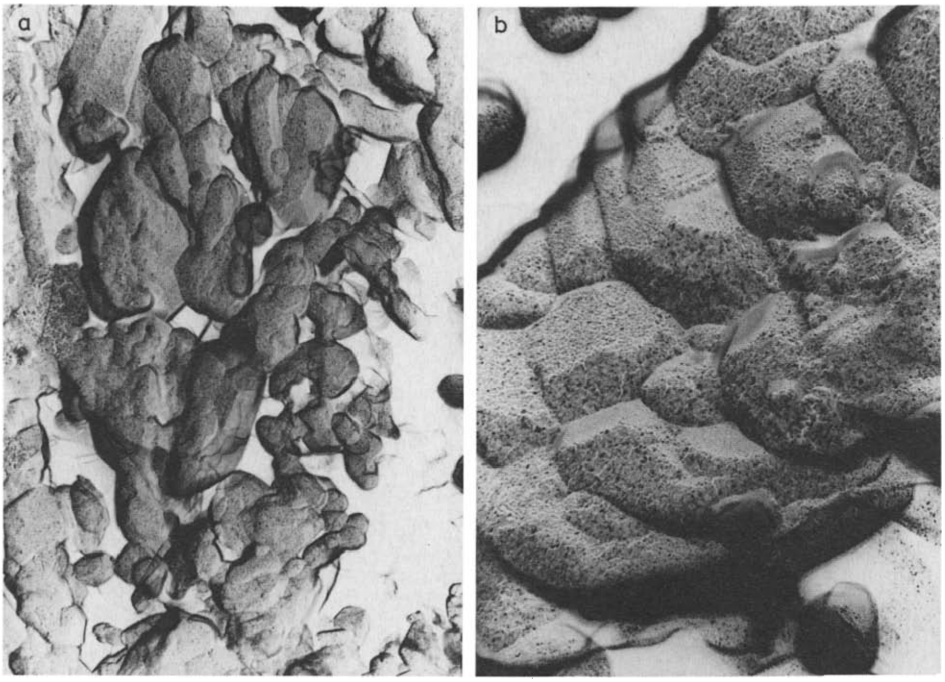

Fig. 3. Electron microscopy of face (001) in the earlier stages of $Na_3P_3O_9 \cdot 6H_2O$ dehydration in a flow of nitrogen ($t = 40$–$45°C$; $\Delta m < 0.1$ mol H_2O): (a) ×21000; (b) ×67500.

fine crystal sample (Fig. 2) stronger self-acceleration is observed due to summing up of the two effects: consecutive commencement of reaction of crystal faces and of individual crystals.

Figure 4 gives, for comparison, the kinetic curve (1) of a powder-like sample, the dehydration of which is also characterized by strong self-acceleration. In this case, along with the above reasons for self-acceleration, one should also take into account the fact that during grinding the sample loses

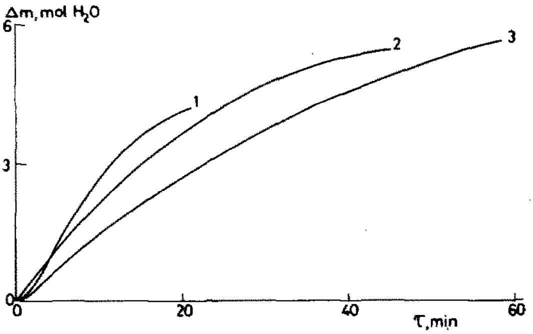

Fig. 4. Kinetic curves of $Na_3P_3O_9 \cdot 6H_2O$ dehydration in a flow of nitrogen at 43°C: (1) powder, $D = 0.01$–0.02 mm, $m = 8.31$ mg; (2) single crystal, $m = 2.45$ mg; (3) single crystal, $m = 7.95$ mg.

TABLE 1

Kinetic characteristics of $Na_3P_3O_9 \cdot 6H_2O$ dehydration in flowing nitrogen

$D = 0.05$–0.1 mm			$D = 0.01$–0.02 mm		
t (°C)	n	Δm_{max} (mol H_2O)	t (°C)	n	Δm_{max} (mol H_2O)
40	1.5	1.9	35	2.1	1.6
42	1.5	1.4	38	1.7	1.4
45	1.5	1.5	40	1.8	1.3
47	1.2	1.2	43	1.6	1.2
50	1.3	1.3	45	1.7	1.3
55	1.3	1.1	50	1.6	1.3

part of its crystal water and dehydration begins on a partially dehydrated surface. The powder-like sample differs from other samples in the termination of its dehydration kinetic curves (Fig. 2). These curves end at $\Delta m = 4$–4.5 mol H_2O.

Changing self-acceleration degree as a result of granulometry change is reflected in the value of the kinetic parameter, n, in the equation $\alpha = 1 - \exp(-k\tau^n)$ (α = dehydration degree; k = constant), which satisfactorily approximates the experimental kinetic curves (Table 1). The kinetic parameter increases on transition from single crystal ($n = 1.0$ at 43°C) to fine crystalline samples ($n = 1.5$ at 42°C) to powder-like samples ($n = 1.6$ at 43°C). The amount of water, Δm_{max}, lost at the moment of maximum reaction rate (from $\Delta m_{max} = 0.5$ mol H_2O to $\Delta m_{max} = 1.1$–1.9 mol H_2O) increases in the same order.

CONCLUSIONS

Isothermal dehydration of $Na_3P_3O_9 \cdot 6H_2O$ single crystals and polycrystalline samples in flowing nitrogen at 35–60°C proceeds as a reversible topochemical process with an induction period, reaction rate build-up with time and with the reaction rate passing through a maximum. The kinetic characteristics of this reaction are sensitive to granulometry and to partial water vapour pressure over the substance. Under conditions of uniform localization self-acceleration increases from single crystals to polycrystals, which is explained by the crystal faces and also of individual particles of polycrystalline samples beginning to react.

REFERENCES

1 E.A. Prodan, V.M. Galogaža, T.N. Galkova and S.I. Pytlev, Zh. Fiz. Khim. 55 (1981) 2653 (in Russian).

2 E.A. Prodan and S.I. Pytlev, Zh. Fiz. Khim., 57 (1983) 1998 (in Russian).

3 E.A. Prodan and S.I. Pytlev, Izv. Akad. Nauk SSSR, Neorg. Mater., 20 (1984) 628 (in Russian).

4 H.M. Ondik and J.W. Gryder, J. Inorg. Nucl. Chem., 14 (1960) 240.

5 J. Tordjman and J.C. Guitel, Acta Crystallogr., Sect. B, 32 (1976) 1871.