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KINETICS OF SOLID- AND LIQUID-PHASE REACTIONS IN PHOSPHATE SYSTEMS

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ABSTRACT

The results of isothermal and non-isothermal studies of reactions in inorganic phosphate systems have been reviewed on the basis of comparison of kinetic data for chemical processes, taking place in solid phase and in aqueous solutions, in amorphous and crystalline phases, on the surface and inside the crystals.

INTRODUCTION

The interest attached to the solid-phase and liquid-phase reactions in phosphate systems is determined by various circumstances. These reactions comprise some features inherent to chemical transformations of inorganic, organic and biological objects. They can proceed according to a scheme of localized reactions, including various types of uniform and spot localization forms, and according to a scheme of delocalized solid-state reactions. In the latter case, if a single crystal is the object of analysis, the reaction proceeds with about the same probability in any point on the surface and inside the crystal. This is characteristic for the process of intrinsinc hydrolysis during thermal treatment of sodium cyclotriphosphate monohydrate, $Na_3P_3O_9 \cdot H_2O$.

At precipitation of salts from aqueous solutions in phosphate systems and at mechanical activation of protonated salts oil-like, plasticine-like or rubber-like substances are formed, the state of which can be considered as intermediate between solid and liquid. In this state the reactivity of the substance is quite different as compared to the reactivity of the same substance in crystalline state and in aqueous solution. Investigation of reactions in phosphate systems allow to obtain comparable data on reactivity of one and the same substance in various aggregation states.

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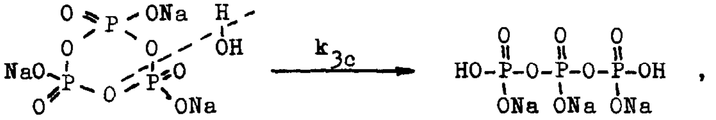
RESULTS AND DISCUSSION

Notwithstanding the identity of crystal structures of $Na_3P_3O_9$ and $Na_3P_3O_9 \cdot H_2O$ thermal dehydration proceeds not by direct transition of monohydrate crystal lattice into the crystal lattice of anhydrous salt, but through an intermediate stage of initial crystal destruction and of anion cycle rupturing [1]. Ring rupturing takes place according to the scheme of intrinsinc hydrolysis



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where k_{3c} is the first order solid-state decyclization rate constant. From the temperature dependence for k_{3c} (Fig.1) a value of

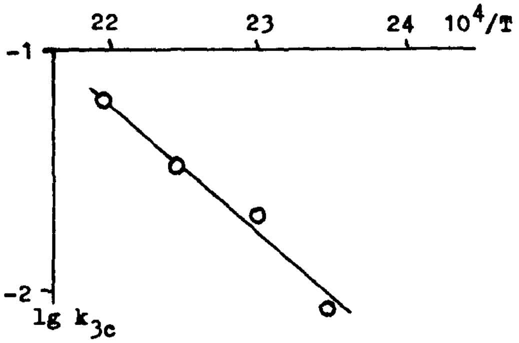

Fig.1 Temperature dependence for k_{3c} (isothermal treatment of $Na_3P_3O_9 \cdot H_2O$ in dry ammonia atmosphere at p_{NH_3}=930 nPa)

effective activation energy is calculated (E=93 kJ/mol) which coincides with the known values E=84-100 kJ/mol for the cyclotriphosphate hydrolysis in aqueous solutions [2]. Such a coincidence does not mean that the two decyclization processes (in solid state and in aqueous solutions) are identical. The solid-state decyclization possesses some peculiarities, for instance, the thermal treatment of $Na_3P_3O_9 \cdot H_2O$ should be carried out in ammonia atmosphere. At thermal treatment in vacuum the first order law is not obeyed to.

Thermal conversions of $Na_3P_3O_9 \cdot H_2O$ represent a case when the reaction is delocalized or uniformly localized inside the crystal. Another localization form - spot localization inside the crystal - is represented by thermal transformations of $MnHPO_4 \cdot 3H_2O$ [3]. In this case two parallel reactions occur

$MnHPO_4 \cdot 3H_2O(cryst.) \rightarrow MnHPO_4 \cdot 0.5H_2O(amorphous) + 2.5H_2O \uparrow$,

$5MnHPO_4 \cdot 3H_2O(cryst.) \rightarrow Mn_5H_2(PO_4)_4 \cdot 4H_2O(cryst.) + H_3PO_4(liq.) + 11H_2O$,

where the first one is dehydration (A) and the second one is disproportionation (B). The relation between the reactions (A) and (B) as a function of temperature and water vapour pressure is shown in Fig.2. At high t and low p_{H_2O} dehydration prevails, at

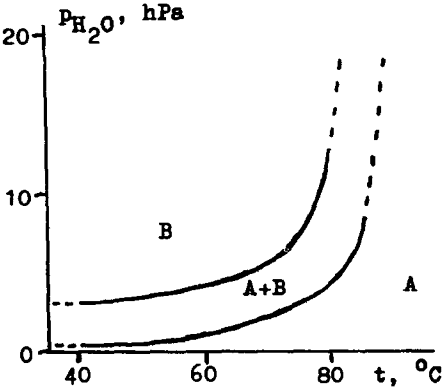

Fig.2 Regions where reactions (A) and (B) prevail (isothermal treatment of freshly obtained $MnHPO_4 \cdot 3H_2O$ crystals, τ=1-8 h)

low t and high p_{H_2O} prevails disproportionation. Dehydration is always localized on the crystal surface. Depending on t and p_{H_2O} disproportionation is localized on the surface or inside the crystal. Under conditions given in Fig.2 disproportionation is localized inside the crystal.

Dehydration of $Na_3P_3O_9 \cdot 6H_2O$ at moderate air humidity ($r < 50\%$) and in vacuum in contrast to dehydration of $Na_3P_3O_9 \cdot H_2O$ takes place without decyclization

$Na_3P_3O_9 \cdot 6H_2O(cryst.) \longrightarrow Na_3P_3O_9(cryst.) + 6H_2O \uparrow$.

Under severe dehydration conditions (in vacuum, at low r values) typical is the uniform surface localization form and the crystal faces react in order of decrease of their activity: first (100), then (001) and (010). At the increase of r uniform localization gradually changes into spot localization, which prevails at $r > 30\%$.

On the basis of the known kinetic model [4] a formula for the conversion of a triclinic crystal according to the scheme of uniform surface localization is derived [5]

$$\alpha = 1 - \frac{\left[a_0 - v_a(\tau - \tau_{ind}^{(100)})\right]\left[b_0 - v_b(\tau - \tau_{ind}^{(010)})\right]\left[c_0 - v_c(\tau - \tau_{ind}^{(001)})\right]}{a_0 b_0 c_0}, \quad (1)$$

where α is conversion degree; a_0, b_0, c_0 are the halves of lateral lengths of initial crystal along a, b, c directions respectively; v_a, v_b, v_c are the linear velocities of flat reaction front advance in the same directions; τ is the time; $\tau_{ind}^{(100)}$, $\tau_{ind}^{(010)}$, $\tau_{ind}^{(001)}$ are the induction periods that precede the entry into reaction of the corresponding crystal face.

Analysis of Eq.(1) with the use of an ES-1036 computer shows that depending on $\tau_{ind}^{(100)}$, $\tau_{ind}^{(010)}$, $\tau_{ind}^{(001)}$ values and on relations among v_a, v_b, v_c velocities the topochemical process takes place without self-acceleration, with one-fold or multi-fold self-acceleration. This conclusion meets the experimental data for dehydration of $Na_3P_3O_9 \cdot 6H_2O$ crystals [6].

Different stages of thermal decomposition reactions have different sensitivities to the aggregation state of the substance. Crystalline salt $NH_4Mg_2P_3O_{10} \cdot 6H_2O$ as compared to amorphous salt $NH_4Mg_2P_3O_{10} \cdot 7H_2O$ releases hydration water more slowly at the initial stages of dehydration and more rapidly at the final stages. This is explained by various physical properties of the resulting products. Both salts have been precipitated in the system $(NH_4)_5P_3O_{10}$-$MgSO_4$-H_2O which is characterized by a decrease of chain triphosphate degradation velocity in following sequence: oily phase, amorphous phase, aqueous solution, crystalline phase. In solid phase (frozen solution) the velocity of $H_3P_3O_9$ cycle rupturing is also higher than in aqueous solution. These cases represent a variant of the Hedvall effect, when the reactivity abruptly changes in the vicinity of phase transition temperature.

REFERENCES

1 H.M.Ondik, Acta Cryst., 18 (1965) 226
2 E.A.Prodan, L.I.Prodan and N.F.Ermolenko, Tripolifosfaty i Ikh Primenenie (Tripolyphosphates and Their Use). Publ. Nauka i Tekhnika, Minsk, 1969, 533 pp. (In Russian)
3 V.V.Samuskevich and E.A.Prodan, Dokl. Akad. Nauk BSSR, 28 (1984) 1016 (In Russian)
4 B.Delmon, Introduction à la cinétique hétèrogéne. Éd. Techn., Paris, 1969, 695 pp.
5 E.A.Prodan, Bull. Soc. chim. Beograd, 49 (1984) 291
6 E.A.Prodan and S.I.Pytlev, Izv. Akad. Nauk SSSR, Neorg. Mater., 19 (1983) 639 (In Russian)