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KINETICS AND MECHANISM OF TOPOCHEMICAL TRANSFORMATIONS OF PHOSPHORIC SALTS

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Abstract

A study was made on the topochemical processes of hydration-dehydration, ammonation-deammonation, disproportionation and anionic condensation (certain of which can proceed concurrently) that occur during the production, storage and exploitation of phosphoric salts and phosphate materials. These processes which can be accompanied by complicated structural transformations and sometimes by melting were shown to be satisfactorily described by the known kinetic regularities. The detected deviations, that are associated with the anomalous influence of temperature, the gaseous phase, the size and habit of the crystals and the ageing of samples on the process rate, were explained in terms of the localization peculiarities of the reactions proceeding on the surface or in the bulk of the reactant.

Keywords: kinetics, localization, phosphoric salts, topochemical reactions

Introduction

The unusual variety and complexity of topochemical reactions have not yet allowed the creation of a unified theory similar to the molecular-kinetic theory of homogeneous reactions. To date, therefore, the progress in topochemistry is accounted for by the accumulation of new experimental data and the establishment of factors determining the peculiarities of localization and kinetics of topochemical processes and the nature of the revealed regularities. Unfortunately, the sphere of the objects and reactions being studied is rather narrow. We reasoned that the results of systematic investigations of the kinetics and mechanism of topochemical transformations of phosphoric salts, which were undertaken by us to clarify certain questions of the chemistry and technology of these compounds, would be of interest from the aspect of topochemistry [1–7]. They can be useful, in particular, in the discussion of such problems as:

- the correlation (or its absence) between the kinetics and the localization character of the isothermal reaction;
- the localization of the reaction in the bulk of the initial crystal;
- the morphology of the reaction zone;

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- the orientation effects at the interface, epitaxial and topotaxial growth of a solid product;
- metastable states and the possibility of an isothermal reaction in the autooscillatory regime;
- the features of reactions limited by the stage of proton transfer within the proton hydrate sub-lattice of initial crystal.

The dissimilar topochemical reactions (consecutive and parallel) take place in the course of production, storage and exploitation of phosphoric salts and phosphate materials. They include specific reactions that are characteristic only of this class of compounds, e.g. the disproportionation and anionic condensation of acidic salts, and the hydrolytic degradation of condensed phosphates, accompanied by reorganization of the phosphate anion. Concurrently (or independent of them), the reversible reactions of hydration-dehydration, ammonation-deammonation and thermal decomposition (which bear a common character) take place.

Both reaction types are localized on the surface or in the bulk of the initial crystals and are of a topochemical nature. It was of interest to clarify as far as the known regularities observed during the study of simple model reactions can be used to such complicated systems.

The stability and reactivity of phosphoric salts essentially depend on the size and habit of the initial crystals, the production and storage conditions, the temperature and the composition of the gaseous medium. All these factors were strictly fixed during the kinetic investigations. In order to acquire comprehensive information about the process, the kinetic data were obtained by different methods. Gravimetric data characterize the process of release of gaseous products (or absorption of gaseous reagents), optical microscopy gives information about the character of the reaction localization, and X-ray diffraction analysis permits to fix the disappearance of the initial phase and the accumulation of the product phase. The experimental data were processed with the generalized equation of topokinetics $\alpha=1-\exp(-k'\tau^{n})$, where α is the conversion degree, τ is the time, n is a kinetic parameter and k' is a constant connected with the rate constant k by the equation $k=n(k')^{1/n}$. The kinetic parameter indicates whether the reaction proceeds in the kinetic ($n\geq1$) or the diffusion regime ($n=0.5$), and at $n>1$ it can also be used for a qualitative assessment of the extent of reaction localization on the surface of the initial crystals [8].

Localization and kinetics of isothermal reactions

Through the example, let us consider the isothermal dehydration of $MnHPO{\cdot}3H_2O$ crystals [9]. At first glance, the kinetics and mechanism of the process are not remarkable. The curves of the transformation degree (α) *vs*. time (τ) both in vacuum and in a water vapor atmosphere are S-like in shape (n=1.3–1.5) that agrees well with the reaction localization observed on the crystals surface. These curves are practically coincident in α *vs*. $\tau/\tau_{0.5}$ coordinates. This fact testifies that the process mechanism varies only slightly with the temperature and the gaseous phase composition.

However, it must be borne in mind that the observed correlation of the kinetics and the localization character is not so evident as might have appeared at first glance. The point is that, according to results of XRD analysis, even the complete consumption of the initial trihydrate phase is not accompanied by the formation of a crystalline product. The starting crystals not only retain their habit, but also exhibit high mechanical strength, which points to the formation of a stable pseudomorph. According to the data obtained earlier during studies of the dehydration of zeolite [10, 11] and hydrated carbonates [12], the formation of the pseudomorph must result in the serious diffusion hindrances of the process. Their absence in the case being considered is due to the layered structure of the trihydrate. Removal of the crystallization water out of the interlayer space results in the formation of a developed system of transport pores as indicated by an increase in the specific surface from 0.1 to 35 $m^2 g^{-1}$. The same model is realized during the dehydration of the majority of phosphates independently of the character of attendant structural transformations. The α *vs*. $\tau/\tau_{0.5}$ kinetic curves of the dehydration of $MnKPO_4{\cdot}H_2O$ and $Mn(H_2PO_4)_2{\cdot}2H_2O$ practically coincide among themselves (n=2.2–2.5) and correlate with the S_s–$\tau/\tau_{0.5}$ curves [1], although in the former case dehydration proceeds by the zeolite mechanism and in the latter case it is characterized by the nidus localization and the formation of a well-crystallized anhydrous salt.

This is not to say that for phosphates the interrelation between the localization character of topochemical transformations and their kinetics is entirely absent. Every so often the appearance of the reaction figures coincides precisely in time with separation of kinetic curves off the axis of abscissas, and a total covering of the crystals surface by these figures coincides with the α_{max} value (the time corresponding to the maximum rate ν_{max}). Such agreement have been noted by us for reactions of various type accompanied by the formation of crystalline product (thermal dehydration of $Mn(H_2PO_4)_2{\cdot}2H_2O$ [13], disproportionation of $Zn(H_2PO_4)_2{\cdot}2H_2O$ under the layer of organic solvent [14], formation of $Pb_5(PO_4)_3OH$ in the course of lead sorption by hydroxyapatite from aqueous solution [15]) and even in those cases when the product is amorphous (dehydration of $Mg(H_2PO_4)_2{\cdot}4H_2O$ [16]).

Comparing the kinetic data obtained by optical and gravimetric methods, it is well to bear in mind that the outlines of figures on a surface of reacting crystal sometimes do not coincide with the reaction zone. We already mentioned the absence of any visible changes of $MnKPO_4{\cdot}H_2O$ crystals after their total dehydration. Other extreme case is possible also when the figures arise and grow prior to the beginning of the reaction, that has been connected with the appearance of cracks in the crystal as the result of enhancing strains at its heating up to temperature of the experiment. The intermediate variant is more often realized, at which structural transformations slightly lag behind (with space and time) chemical reaction but the observed picture of localization partly correlates with the kinetic data obtained by other methods, in particularity, gravimetry. During studies of the isothermal dehydration of $ZnHPO_4{\cdot}H_2O$ in vacuum [17] it was shown, that gravimetric kinetics can adequately describe the real process, even though it absolutely does not correlate with the reaction localization observed on the individual crystals. The α *vs*. τ curves in this case account for the sequence of entry into reaction of the individual crystals. This is associated with difficulty of nucleation, which limits the process being investigated. As a result, both shape of a kinetic curve and the localization character of the process reflect distribution of active centers in investigated group of crystals. In some cases the interrelation between a kinetics and localization of the studied reaction is disturbed because of influence of attendant chemical processes. So, the kinetic curves of $Co_3(PO_4)_2 \cdot 8H_2O$ dehydration in the water vapor atmosphere have the parabola shape, in spite of the clearly pronounced nidus localization of this processes. The diffusion difficulties of the process are due to the fact, that the liberation of crystal water in the volume of crystal is accompanied by anionic condensation.

The proceeding of reaction in diffusion regime is characteristic both of the processes of anionic condensation and of attendant reactions, in particular, of dehydration and deammonation of metalammoniumphosphates [18, 19]. From this viewpoint the data about dehydration of KH_2PO_4 crystals as a result of their anionic condensation were rather unexpected. In this case, the unusual localization characterized by preferential propagation of reaction into the crystal bulk by not solid front and selectively along certain branching planes [20] was noted. S-like in form kinetic curves agree with such model. The possibility of realization of this mechanism is due to the block structure of KH_2PO_4 crystals. The portions of acceleration in the kinetic curves correspond to branching of the reaction along the inter-block boundaries. The subsequent deceleration is connected with expense of active inter-block substance and with necessity of the reaction penetration into the depths of blocks.

All the more complicated kinetics with stages of the reaction stop and its subsequent acceleration was observed in the course of isothermal dehydration of $Zn(H_2PO_4)_2 \cdot 2H_2O$ [21] and $MnHPO_4 \cdot 3H_2$ [22]. The complex run of α *vs.* τ curves is due to the partial absorption of liberated water by phosphoric acid, which is formed as a result of disproportionation of these acidic phosphates. The disproportionation reaction of acidic phosphoric salts accompanied by the formation of less-proton phosphate and phosphoric acid is characterized by unusual variety of the localization forms depending on the experimental conditions [8]. Let us point out only the most interesting type connected with the reaction localization in the bulk of the initial crystals. The disproportionation of $MnHPO_4 \cdot 3H_2O$ starts in three-dimensional defects and develops at the expense of the growth of the solid product crystals (or by a topotaxical model ‘crystal in crystal’ or in the volume of the growing gas–liquid–solid inclusion). If this inclusion makes it to the external crystal surface, the vapor pressure of water (which initiate process of disproportionation) in it falls off and process is stopped at small degrees of transformation. The fluctuation in concentration within the same crystal and relative stability of metastable states can result in the more complicated kinetic effects, in particular, the proceeding of the isothermal-isobaric reaction in auto-oscillatory regime. In this case, removal of water vapor through the layer of the unreacted crystal has the feature: the diffusion process proceeds with acceleration.

Temperature effect

The kinetic curves of topochemical transformations of phosphoric salts obtained at different temperatures every so often coincide in α *vs*. $\tau/\tau_{0.5}$ coordinates. The Arrhenius energy of activation E_v or E_k and pre-exponential factor A can be calculated from the temperature dependence of the reaction rate v or the rate constant k which, as a rule, is satisfactorily approximated by a straight line. Unfortunately, even in this case a physical sense of obtained values is not always clear; they can be used only for comparison of reactivity of the substances under study. What is more complex to interpret the Arrhenius characteristics, if form of the kinetic curves and the value of the kinetic parameter n changes with temperature. All the same time, the thorough kinetic analysis (first of all the comparison of the kinetic characteristics obtained at different temperatures with observed localization of the reaction) permits to establish in many cases the sufficiently fine variations in the process mechanism. In studies on dehydration of $Mg(H_2PO_4)_2{\cdot}4H_2O$ single crystals in vacuum [23] the kinetic parameter n reduces from 2.7 to 1.8 with the increase in temperature. This effect reflects a change in the nucleation-to-growth rate ratio. Visually, this is manifested as an increase in the number of the reaction centers. Since the α_{max} value is not changed, it may be suggested that the reaction is propagated through the crystal anisotropically. As temperature increases, the predominant propagation (or branching) of the reaction into the crystal bulk along extended defects makes a gradually increasing contribution to the observed acceleration of the process. Over part of the limit these changes in the dehydration mechanism are not radical and are not exhibited on the Arrhenius plot (though, probably influence its slope), but at the attainment of a certain temperature result in a drastic change of the process character: a scarp deceleration of the isothermal reaction is observed instead of acceleration (n falls off respectively to 0.5). As a result, monotonous variation of the reaction rate with the temperature is disrupted and the Arrhenius plots show discontinuity. The observations on the crystals during of isothermal reaction have demonstrated that the diffusion hindrances were connected with the formation of a liquid phase. Its appearance in case of reversible topochemical reaction proposes not only preference propagation of reaction into the depths of the crystal, but also the fulfilment of a number of other conditions, in particular, the presence not far from the reaction zone of three-dimensional defects, the partial disturbance of the process reversibility, the solubility of reagent or product in water. All these conditions are realized in the case being considered.

For phosphates the influence of temperature as factor stimulating the structural regulation of the transformation products is not determining. Therefore, the temperature anomalies connected with the formation of pseudomorph (similar to those, which have been detected by us in studies of the dehydration process and thermal decomposition of lanthan carbonate octahydrate [8]) were not fixed. The fractures or disruptions on the Arrhenius plots revealed in some cases, as a rule, are due to an imposition of attendant processes. So, for example, the anomalous change of the dehydration rate of $CoNH_4PO_4{\cdot}H_2O$ with temperature is caused by formation and crystallization of the product of parallel reaction of anionic condensation.

Effect of gaseous product

Almost all studied transformations of phosphates are reversible, therefore, influence of the gaseous (or liquid) product frequently plays a crucial role. In accordance with the Bretsznajder–Zawadski regularities the increase of pressure of a gaseous product, as a rule, causes the enhancement of the Arrhenius activation energy E_k (or E_v) that is compensated by a rise of pre-exponential factor A and a displacement of the ΔT region sideways of high temperatures. If the reversibility in the reacting system is disrupted, the influence of gaseous product is more diverse, that is reflected on the form of kinetic curves and character of the temperature dependence of the reaction rate.

A liberation of water from the sample during the isothermal heating of $Mg(H_2PO_4)_2{\cdot}2H_2O$ small-crystals [24] is accompanied by formation of amorphous product but, in doing so, the process is free from diffusion difficulties. In vacuum the reaction proceeds to completion without any complications but the product resulting in atmosphere of water vapor strongly holds the residual water (0.16 mol H_2O), which can be removed only at significantly higher temperatures simultaneously with the anion condensation. The same effect is observed at dehydration of polycrystalline $Co(H_2PO_4)_2{\cdot}2H_2O$ and $Mg(H_2PO_4)_2{\cdot}4H_2O$ but the quantity of retained water in this case was 0.34 and 1.0 mol H_2O accordingly.

The X-ray amorphous products forming at heating of hydrated magnesium (or cobalt) dihydrogenphosphates in the water vapor atmosphere (p_{H_2O}=20 hPa) after cooling to room temperature intensively absorb the water and are completely liquefied. As the temperature increases and the water vapor pressure decreases, the rehydration rate falls off and the process acquires the solid-state character. In this case the rehydration is restricted to the formation of the starting hydrate, but its crystallization noticeably lags behind the chemical reaction. It results in a peculiar proceeding of isothermal process within certain p_{H_2O} and t region, when after an initial fast absorption of water vapor is observed an appreciable loss of the sample mass. The appearance of a maximum in the Δm–τ curves is explained by the fact that amorphous or poorly crystallized product forming at the high rate of hydration absorbs (because of an elevated reactivity) excessive quantity of a water, which then is released during its crystallization. In spite of essential deviations from equilibrium in $M(H_2PO_4)_2{\cdot}xH_2O$ (cryst.)$\leftrightarrow$$M(H_2PO_4)_2{\cdot}yH_2O$ (amorph)+$(x–y)$ H_2O (vap.) systems under certain conditions the reactions of dehydration-hydration may proceed in cyclic regime. It is necessary to mention the ‘memory’ effect too, when the amorphous products forming at heating of tetra- and dihydrate in spite of like composition at rehydration always restore the lattice of the corresponding starting hydrate.

The kinetic peculiarities of dehydration of $Mg(H_2PO_4)_2{\cdot}4H_2O$ described in the previous section were revealed at different values of water vapor pressure, however the p_{H_2O} can variously influence the process rate within the low- and high-temperature regions. When the solid-state dehydration is predominant, in accordance with the generalities of reversible topochemical reactions, a regular decrease of the dehydration rate is observed as the water vapor pressure increases. At higher temperatures this regularity is upset; moreover, sometimes the opposite effect is observed.

The anomalous influence of water vapor on kinetic characteristics can take place in the cases when the product crystallizes with high rate, as for instance, during dehydration of $ZnHPO_4{\cdot}H_2O$ [25]. The process rate in this case is increased going from vacuum to the water vapor atmosphere in spite of the fact that in both cases the reaction is not experienced the diffusion difficulties (n=1.1–1.4). In doing so the value of the Arrhenius activation energy is not practically changed. Probability, the default of the Bretsznajder–Zawadski regularities is also associated with violation of reversibility in the system, in so far as the anhydrous crystalline zinc hydrogenphosphate obtained from monohydrate is rehydrated with the formation of trihydrate.

The revealed effects of anomalous influence of gaseous product on the kinetic characteristics of thermal transformations of phosphoric salts are due to the change of the process mechanism (from kinetics-controlled to diffusion-controlled or from solid-phase to liquid-phase) and, as rule, are not connected to a manifestation of the Smith–Topley effect.

Influence of other factors

The role of granulometry in majority of discussed cases reduces to variation of the sample surface value that results in the proportional change of the reaction rate. In this situation the activation energy, as a rule, does not vary because according to the Polányi–Wigner equation an increase of the rate constant is compensated principally by variation of the A factor. Topochemical transformations of phosphates for the most part fall in the structure-controlled reactions. The kinetics and the localization character of such processes are mainly determined by the peculiarities of layered lattice of crystals and to a lesser extent depend on their defect structure. Therefore, for instance, after crushing $MnHPO_4{\cdot}3H_2O$ samples [8] reaction of dehydration is only localized on the damage-free surface of the starting crystal and its rate does not change. Under crushing KH_2PO_4 crystals [26] rate increases within of the first 30–40 min and the portion of the induction period in the kinetic curves disappears but then fresh surface is inactivated and the process occurs as well as on the uncrushed sample.

We have already noted by the example of $Mg(H_2PO_4)_2{\cdot}4H_2O$ that the change in the crystal size affects the mechanism its dehydration, but at heating of $Zn(H_2PO_4)_2{\cdot}2H_2O$ in vacuum [21] even the type of transformation is changed: under identical conditions small crystals are subjected to disproportion and large crystals undergo dehydration.

The relationship between rates of these processes also depends on temperature and the water vapor pressure but the most interesting effect is connected with ageing of a sample. The freshly prepared sample of $MnHPO_4{\cdot}3H_2O$ as well as zinc dihydrogenphosphate can be subjected to either dehydration or disproportionation depending on p_{H_2O} but after 2–3 months the second process is not realized. The kinetic analysis shows that with the storage of the trihydrate sample the slope of Arrhenius plots gradually increases without a marked shift of the ΔT region. An increase in the activation energy of the reaction eventually results in impossibility its proceeding. The investigation of the localization process has shown that during the aging of the sample the active centers in the bulk of the starting crystals (on which disporportionation begins) migrate towards the surface, where the conditions for proceeding of reaction are unfavourable.

We have already mentioned that in most cases a change E_k or E_v is compensated by a change of pre-exponential factor A. The compensation effect for isobaric-isothermal reactions is associated at once with the Bretsznajder–Zawadski effect. According to the obtained data this effect can take place also in that case when the changes of Arrhenius parameters are caused by influence of factors which are not associated with reversibility of reaction (the crystal sizes, the ageing of a sample).

Conclusions

The results show that the known generalities of topochemistry are applicable for such complicated reactions as the topochemical transformations of phosphates. The established deviations and anomalies were attributable in terms of the mechanism peculiarities of studied reactions.

The obtained results can serve as the basis for elaboration of modern technology of phosphoric salts and phosphate materials.

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