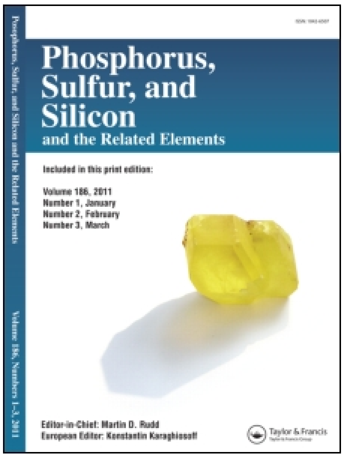

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Topochemistry of Condensed Phosphates

E. A. Prodan[a]
[a] Institute of General and Inorganic Chemistry of the Belorussian Academy of Sciences, Minsk, U.S.S.R.

To cite this Article Prodan, E. A.(1990) 'Topochemistry of Condensed Phosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 109 — 112

To link to this Article: DOI: 10.1080/10426509008040693

URL: http://dx.doi.org/10.1080/10426509008040693

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, pp. 109–112
Reprints available directly from the publisher
Photocopying permitted by license only

TOPOCHEMISTRY OF CONDENSED PHOSPHATES

E.A.PRODAN

Institute of General and Inorganic Chemistry of the Belorussian Academy of Sciences, Minsk, U.S.S.R.

Abstract Some problems concerning structure and reactivity of condensed phosphates, kinetics and mechanisms of reactions of triphosphates in solid and liquid state, synthesis of crystalline salts, chemical activity of crystal faces are discussed.

INTRODUCTION

The performed comparative kinetic study covers two groups of condensed phosphates including triphosphates with different anion structures. The interest attached to the triphosphate compounds is not casual, it is determined by a number of circumstances.

First, these compounds start in fact both homologous series of condensed phosphates with chain-type (polyphosphates) and ring-type anion structures (cyclophosphates). The further members of the series (tetra-, penta-, hexaphosphates and so on) in a specific manner repeat the fundamental properties of triphosphates.

Second, due to an interesting combination of physical and chemical properties they can be obtained as crystalline, amorphous, vitreous, oil-like, and rubber-like substances. In contrast to higher members they are easily crystallized and can be isolated as well characterized individual salts, the purity and properties of which can be controlled and regulated in technological processes.

. Third, as natural compounds they have been subjected to a natural selection, especially the ATP salts. There exists a point of view that reversible cyclization-decyclization processes serve as regulators of the ratio of active (chain) to inactive (cyclic) triphosphate forms. It is of interest to compare the properties of these forms depending on the state of aggregation of substances. The possibility of reproduction of a reversible cyclization-decyclization process in inorganic systems also presents a certain interest.

RESULTS AND DISCUSSION

The reactions investigated include dehydration of triphosphate crystal hydrates and hydration of anhydrous salts, deammoniation of ammonium salts and ammoniation of acid salts, disproportionation of acid salts, anion degradation and anion condensation. Dehydration mechanisms are studied in series of crystal hydrates: of isomorphous double salts of the $Na_3MP_3O_{10}\cdot 12H_2O$ type, where M is Mn, Ni, Cu, Zn; of non-isomorphous sodium cyclotriphosphates $Na_3P_3O_9\cdot xH_2O$, where x is 1, 2, 3; of non-isomorphous salts of lithium, sodium, potassium, ammonium ($Li_5P_3O_{10}\cdot 5H_2O$, $Na_5P_3O_{10}\cdot 6H_2O$, $K_5P_3O_{10}\cdot 4H_2O$, $(NH_4)_5P_3O_{10}\cdot 2H_2O$); of non-isomorphous salts with equal crystal water content ($Na_5P_3O_{10}\cdot 6H_2O$ and $Na_3P_3O_9\cdot 6H_2O$; $Li_3P_3O_9\cdot 3H_2O$ and $Na_3P_3O_9\cdot 3H_2O$). The effect of reaction rate inversion at interaction of commercial and laboratory samples of sodium tripolyphosphate with water vapour is interpreted taking into account the variations of the shape of kinetic curves. Regularities in the shift of thermal stability , of kinetic characteristics of deammoniation, anion degradation, and anion condensation in a line of anhydrous salts - $(NH_4)_5P_3O_{10}$, $(NH_4)_4HP_3O_{10}$, $(NH_4)_3H_2P_3O_{10}$ - are shown to be connected with a topochemical specifity of the reactions studied which are localized on the surface of solids.

Kinetic characteristics of one and the same reaction that proceeds in solid state and in aqueous solutions, in low viscous and high viscous oily phases, in amorphous and crystalline solids, on the surface and in the bulk of crystals, on different crystal faces of a single crystal are compared for one and the same triphosphate compound. For double salts formed in systems of the $(NH_4)_5P_3O_{10}$-$MgSO_4$-H_2O, $(NH_4)_5P_3O_{10}$-$MnCl_2$-H_2O type and for acid salts formed in systems of the $(NH_4)_3H_2P_3O_{10}-Na_3H_2P_3O_{10}-H_2O$, $(NH_4)_3H_2P_3O_{10}-K_3H_2P_3O_{10}-H_2O$ type[1] the following sequence is established in which the rate of anion degradation raises and the stability of linear anion goes down: crystalline phase, aqueous solution, amorphous phase, high viscous oily phase. It should be noted that in contrast to the known rules the degradation rate is higher in solid amorphous phase than in aqueous solution. There is a dehydration oscillatory phenomena connected with consecutive entering of individual crystal faces of a $Na_3P_3O_9 \cdot 6H_2O$ single crystal into the reaction.[2,3]

APPLICATION OF KINETIC DATA

The data on kinetics and reaction mechanisms are not only of theoretical interest, they can be used for solving some practical problems, including the problem of synthesis of new compounds. For chain triphosphates that crystallize from the oily phase and not directly from the aqueous solutions it is of significance whether the compound that should be precipitated had time to crystallize before the start of degradation and before the moment when the oily phase transforms to a vitreous phase. If the rates of crystallization, degradation, and vitrification are known we can choose the precipitation conditions in such a manner that the synthesis can be realized. In this way it is possible to synthesize some crystalline double salts that previously were obtained only in amorphous state, for example, the crystalline $NH_4Mg_2P_3O_{10} \cdot 6H_2O$[4] and its amorphous analogue $NH_4Mg_2P_3O_{10} \cdot 7H_2O$[5] (in literature[6] the amorphous salt $NH_4Mg_2P_3O_{10} \cdot 8H_2O$ is also presented), the crystalline $NH_4Mn_2P_3O_{10} \cdot 5H_2O$[7] and its amorphous analogue $NH_4Mn_2P_3O_{10} \cdot 6H_2O$[5]. It is possible to synthesize some representatives of the new class of crystalline chain acid salts - the trihydrogentriphosphates. These compounds exhibit some interesting properties, for instance, the crystalline $K_2H_3P_3O_{10} \cdot 2H_2O$ at soft mechanical treatment transforms into a plasticine-like substance.

The data on interaction kinetics of crystalline forms of sodium triphosphates with water vapour can be used in granulation technology. In analogous manner the kinetic data on interaction of $K_3H_2P_3O_{10}\cdot H_2O$ and $K_2H_3P_3O_{10}\cdot 2H_2O$ crystal hydrates with gaseous ammonia can be used to produce potassium-ammonium salts. The conditions of synthesis of $Na_5P_3O_{10}\cdot 6D_2O$ crystals and of epitaxially grown crystals of $(NH_4)_5P_3O_{10}\cdot 2H_2O$ are established.

Kinetics and mechanisms of phosphate transformations localized on solid/liquid, solid/solid, and solid/gas interfaces attract attention in connection with phosphorus loss and preservation of the environment when applying fertilizers and phosphorus products. Should the interface processes be put under control it would open some new possibilities for resolving these problems. There are other problems located on the area between phosphorus chemistry and solid state chemistry. Some of them as well as the listed problems are discussed elsewhere.[8]

REFERENCES

1. E.A.Prodan, V.A.Sotnikova-Yuzhik, L.I.Petrovskaya, and V.M.Galogaza, J. Serb. Chem. Soc., 53, 511 (1988).
2. E.A.Prodan and S.I.Pytlev, J. Therm. Anal., 32, 1697 (1987).
3. E.A.Prodan, Reactivity of Solids, 4, 363 (1988).
4. T.N.Galkova and E.A.Prodan, Zhurn. Neorg. Khim., 30, 1400 (1985).
5. O.P.Ol'shevskaya, T.N.Galkova, and E.A.Prodan, Zhurn. Neorg. Khim., 27, 1677 (1982).
6. I.A.Borukhov, R.T.Amineva, and B.M.Beglov, Zhurn. Neorg. Khim., 29, 2534 (1984).
7. T.N.Galkova and E.A.Prodan, Zhurn. Neorg. Khim., 32, 1104 (1987).
8. E.A.Prodan, Neorganicheskaya Topokhimiya - Inorganic Topochemistry (Nauka i Tekhnika, Minsk, 1986), Chapt.3, pp.50-72, Chapt.6, pp.121-160.