

## **TOPOCHEMICAL TRANSFORMATIONS OF CYCLOTRIPHOSPHATES OF ALKALI METALS AND AMMONIUM**

*S. I. Pytlev*

INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY OF THE ACADEMY OF  
SCIENCES OF THE BSSR, MINSK, USSR

The isothermal and nonisothermal conversions of hydrated and anhydrous forms of cyclotriphosphates of sodium, lithium and ammonium were investigated in different gaseous atmospheres and in vacuum. It was shown that gaseous ammonia in its mixtures with water vapour can accelerate the solid-state splitting of the anionic cycle. A mechanism is suggested for the decycling effect of gaseous ammonia and its mixtures with water vapour.

Despite the large number of publications on the transformation of condensed phosphates, the literature contains practically no information on the influence of temperature and the gas atmosphere composition on the process of the solid-phase decyclization of cyclic triphosphate anions. This report describes a study of the topochemical transformations of the cyclic triphosphates of sodium,  $\text{Na}_3\text{P}_3\text{O}_9 \cdot x\text{H}_2\text{O}$  ( $x = 1, 3, 6$ ), lithium,  $\text{Li}_3\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$ , and ammonium,  $(\text{NH}_4)_3\text{P}_3\text{O}_9$ , in an atmosphere of air, in vacuum, in ammonia and in mixtures of ammonia and water vapour.

When heated in vacuum, in a water vapour atmosphere or in air, sodium cyclotriphosphate tri- and hexahydrate lose crystalline water, mainly below  $100^\circ$ , the hexahydrate under going dehydration without anion ring breakage and without crystallization of the intermediate phases, while for the trihydrate there is similarly no ring breakage, but the intermediate monohydrate undergoes crystallization.

When the monohydrate is heated under the same conditions, water is removed at above  $100^\circ$ , in two stages, with corresponding endoeffects at 128 and  $210^\circ$ . Within the given temperature range, and especially in the second stage, the dehydration is accompanied by decyclization of the anion, which results in amorphous products. The decomposition degree is comparatively low, the content of phosphorus in the cyclotriphosphate form not falling

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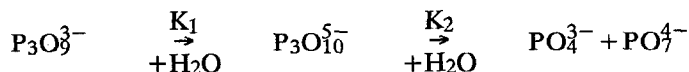
below 88 %. With further temperature increase, recondensation of the anion cycle decomposition products takes place and the final product is chromatographically pure sodium cyclotriphosphate.

The crystallohydrates act otherwise when heated in an ammonia atmosphere. Below 100°, because of the protecting gas jacket effect, the *m-t* curves for the tri- and hexahydrate shift towards higher temperatures. For the monohydrate, as previously, the reaction is at first not sensitive to the gas pressure, but later, starting from 170°, instead of the mass loss in a certain temperature range there is a mass gain and the thermogravimetric curve passes through a maximum. The increase in mass in the interval between the maximum and minimum is due to the ammonization of the acid products of anion ring breakage by gaseous ammonia.

The dehydration curves of sodium cyclotriphosphate tri- and hexahydrate also pass through a minimum, the appearance of which is connected with decomposition of the intermediate monohydrate. According to the X-ray data, the latter crystallizes out of the anhydrous product of dehydration of the initial crystallohydrates in the atmosphere of released water vapour. The regular increase in the triphosphate cycle decomposition degree in the sequence mono-, tri-, hexahydrate is connected with the fact that this is the sequence of increase in the quantity of water vapour released, and of the increase in its partial pressure over the crystallohydrate.

The effect of the anion cycle splitting during the thermal treatment in gaseous ammonia or its mixtures with water vapour is characteristic for the lithium and ammonium salts too. The changes in the anion composition in these cases do not comprise the simple transformation of the cyclotriphosphate into the chain triphosphate. Even in the early stages of the decyclization, the samples contain not only the chain triphosphate, but also products of the decomposition of the chain and anion condensation. The latter comprise the fraction of polyphosphates which have more than five phosphorus atoms in the chain or cyclic anion. The proportion of this fraction increases with the increase of temperature or of the duration of thermal treatment.

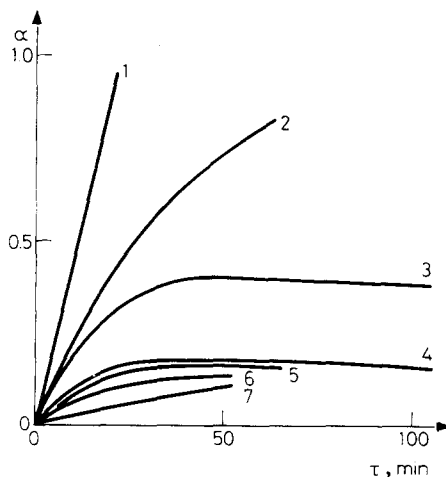
The solid-phase decyclization kinetics was studied by means of TLC on the examples of  $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$  and  $\text{Li}_3\text{P}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  in an atmosphere of dried ammonia ( $P_{\text{NH}_3} = 930 \text{ hPa}$ ,  $t = 122\text{-}182^\circ$ ). In the interval of the thermal conditions used, the solid-phase hydrolysis process can be illustrated by the following scheme:



where  $K_2 > K_1$ , due to which chain sodium triphosphate does not accumulate in the decyclization products.

As in the case of aqueous solutions, the anion ring breakage kinetics in the solid phase during the thermal treatment of  $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$  is described satisfactorily by the equation of first-order reactions. As calculated from the thermal dependence of the rate constant, the effective activation energy of the solid-phase anion decyclization,  $E = 93$  kJ/mol, does not exceed the limits of  $E = 84\text{--}100$  kJ/mol given in the majority of literary sources for decyclization of the cyclotriphosphate ion in aqueous solution [1].

In the case of lithium cyclotriphosphate trihydrate, the process of solid-phase anion decyclization is complicated by the anion condensation reactions, which occur at a significant rate in the temperature interval used. The complex composition of the products formed and their catalytic effect on the triphosphate cycle breakage rate explain the fact that the decyclization kinetic for lithium cyclotriphosphate trihydrate is not described by the simple equation of first-order reactions (kinetic parameter  $n$  being 1.24–1.69). For the same reason, the effective activation energy  $E = 153$  kJ/mol found from the temperature dependence of the solid-phase decyclization rate constant exceeds the bounds of the values found for hydrolysis of the cyclotriphosphate ion in aqueous solution.



**Fig.1** Influence of the gas atmosphere composition on the solid-state decyclization kinetics during the thermal treatment of  $\text{Na}_3\text{P}_3\text{O}_9 \cdot \text{H}_2\text{O}$ . 1 -  $p_{\text{NH}_3} = 906$  hPa,  $p_{\text{H}_2\text{O}} = 24$  hPa, 2 -  $p_{\text{NH}_3} = 930$  hPa, 3 -  $p_{\text{NH}_3} = 133$  hPa,  $p_{\text{air}} = 800$  hPa, 4 -  $p_{\text{NH}_3} = 133$  hPa, 5 -  $p_{\text{NH}_3} = 112$  hPa,  $p_{\text{H}_2\text{O}} = 23.4$  hPa, 6 -  $p_{\text{H}_2\text{O}} = 23.4$  hPa, 7 - vacuum,  $p = 10^{-2}$  hPa

Study of the effect of the gas atmosphere composition on the rate of triphosphate cycle splitting in the solid phase revealed that gaseous ammonia, especially when combined with water vapour, speeds up the anion ring breakage considerably (Fig. 1). The decyclization rate is the higher, the higher the absolute ammonia pressure or its partial pressure in mixtures with water vapour (curves 1 and 5) or with air (curve 3). Water vapour itself does not influence the ring breakage kinetics significantly, but it intensifies the decyclizing effect of gaseous ammonia.

Comparison of the results with those obtained during an electrochemical study of the process allowed an explanation of the decyclizing effect of gaseous ammonia and its mixtures with water vapour: a shift in the crystallohydrate water dissociation equilibrium for the solid reagent structure. It should be pointed out that, as no triphosphate cycle breakage was observed during thermal treatment of anhydrous crystalline sodium cyclotriphosphate in gaseous ammonia and its mixtures with water vapour, the important role in the occurrence of the decyclization process in the solid phase is played by the activation of the anion cycles in the first stage of dehydration.

## References

- 1 E. A. Prodan, L. I. Prodan and N. F. Ermolenko, *Tripolifosfaty; Ikh Primenenie (Triphosphates and Their Use)*, Nauka, Minsk, 1969, p. 533.

**Zusammenfassung** — Isotherme und nichtisotherme Umwandlungen der wasserhaltigen und wasserfreien Formen von cyclischen Natrium-, Lithium- und Ammoniumtriphosphaten wurden in verschiedenen Gasatmosphären und in Vakuum untersucht. Es wurde gezeigt, daß gasförmiges Ammoniak und dessen Gemische mit Wasserdampf die Aufspaltung der Anionenringe im Festzustand zu beschleunigen in der Lage sind, und hierfür das Schema für einen Reaktionsmechanismus entwickelt.