CHEMICAL SCIENCES

THE PROCESS AND PRODUCTS OF INTERACTION IN THE PHOSPHORUS OXIDE–WATER SYSTEM

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Abstract

Experimental results have confirmed that, depending on the phosphorus concentration in the P_4O_{10}–H_2O system, condensed phosphoric acids with various anionic structures are formed – either linear (with a degree of polycondensation n = 2–9) or cyclic (n = 4). The duration of the degradation process in the P_4O_{10}–H_2O system has been evaluated. A contemporary scheme for the hydration process of P_4O_{10} has been proposed.

Keywords: interaction, hydration, degradation, anion structure, condensed phosphoric acids, linear, cyclic.

1. Introduction

Due to the inherent anomalies of water, the mechanisms of many chemical reactions involving it are complex and remain insufficiently understood. In recent years, the understanding of the stepwise nature and mechanisms of dehydration reactions of numerous inorganic salts has undergone fundamental revision [1, 2].

Equally complex are the processes associated with the hydration reactions of inorganic compounds. The interaction of H_2O with highly hygroscopic substances such as $TiCl_4$ or P_4O_{10} is accompanied by intricate chemical transformations. However, the description of the sequential stages of these typically multistep processes remains poorly substantiated.

Works devoted to the study of phosphorus(V) oxide hydration [3, 4] describe the assessment of the composition of the condensed phosphoric acids formed and its dependence on the experimental conditions. However, due to experimental difficulties associated with determining the composition of phosphoric acids, they provide contradictory data on the sequence of their formation. The kinetic features of this process have hardly been studied.

According to the established literature [3, 4], the initial stage of P_4O_{10} hydration involves the addition of water to phosphorus(V) oxide, leading to the formation of ultraphosphoric acid with the composition $H_2P_4O_{11}$. Further hydration results in the formation of two forms of cyclotetraphosphoric acid with identical compositions, $H_4P_4O_{12}$ – the "anhydrous" and the "normal" forms.

Later, the authors concluded that the structure of cyclotetraphosphoric acid, in which the hydroxyl groups are evenly distributed among the phosphorus atoms, is more favorable. According to [4], the hydration process of P_4O_{10} can be represented by the following scheme:

$$P_4O_{10} \xrightarrow{+2H_2O} H_4P_4O_{12} \xrightarrow{+H_2O} H_6P_4O_{13} \xrightarrow[-H_3PO_4]{+H_2O} H_5P_3O_{10} \xrightarrow[-H_3PO_4]{+H_2O} H_4P_2O_7 \xrightarrow{+2H_2O} 2H_3PO_4$$

An alternative mechanism for the hydration of phosphorus(V) oxide was proposed in [5]. In this model, ultraphosphoric acid ($H_2P_4O_{11}$) undergoes further hydration, yielding two reaction products – cyclotetraphosphoric and isocyclotriphosphoric acids – both possessing the same overall chemical composition, $H_4P_4O_{12}$.

Subsequent hydration and degradation of each of these cyclic acids lead to the formation of linear polyphosphoric acids, with the maximum number of phosphorus atoms in the chain not exceeding four (tetraphosphoric acid, $H_6P_4O_{13}$).

However, the above-described hydration schemes of P_4O_{10} do not take into account the possible formation

of condensed phosphoric acids containing more than four phosphorus atoms per chain, despite the well-documented existence of highly polymerized phosphoric acids with chain lengths of at least 9–10 phosphorus atoms [1, 2, 6].

The objective of the present work is to investigate the chemical transformations accompanying the interaction within the P_4O_{10}–H_2O system and to clarify the composition of the resulting phosphoric acids.

2. Experimental Procedure

Since the interaction between phosphorus(V) oxide and water is an exothermic process, an aqueous solution of monophosphoric acid (H_3PO_4) of analytical grade ("pure for analysis," containing 63% phosphorus, calculated as P_2O_5) was used as the hydrating medium instead of pure water.

Phosphorus(V) oxide (P_4O_{10}) was gradually added to the acid solution in small portions under constant stirring. The reaction mixture was cooled externally with an ice–water bath. The amount of P_4O_{10} added was calculated so as to obtain a series of mixtures with different total phosphorus concentrations.

Each prepared mixture was then transferred into a desiccator and kept at room temperature with out water vapor of air. To evaluate the kinetics of the hydration process, samples were taken from the reaction mixture at specified time intervals, neutralized with a cooled aqueous ammonia solution, and analyzed.

Given the presence of high–molecular–weight acids in the samples, the total phosphorus content was determined gravimetrically using the quinolinium molybdate method (relative error ±0.2%) after their complete conversion to monophosphoric acid. Complete hydrolytic cleavage of the P–O–P bonds, as established in a separate series of experiments, occurred upon heating the aqueous acid solutions at 80–90° C for three hours.

The anionic composition of the condensed phosphoric acids was determined by quantitative chromatographic separation, following a procedure analogous to that described in [2]. The method for determining the anionic composition of the acids was refined in a separate series of experiments. Model samples of mono- and polyphosphoric acids (including pentaphosphoric acid) of known anionic composition were prepared for this purpose.

The concentration of the phosphate anion in the solution applied to the chromatographic origin was maintained within 18–20 μg (as P_2O_5) per 0.1 ml of solution. As the mobile phase for anion separation, an acidic mixture consisting of 58 ml of acetone, 25 ml of a 20% trichloroacetic acid solution, and 17 ml of water was employed.

To prevent degradation, all analyses were performed in a refrigerated chamber at 277–278 K. Quantitative determination of phosphorus in each condensed form was carried out gravimetrically using the quinolinium molybdate method after "wet combustion" in perchloric acid ($HClO_4$).

The results of the anionic composition analysis of the phosphoric acids contained in the control samples are presented in Table 1.

Table 1.

Anionic composition of polyphosphoric acids in model samples

Composition of control sample of polyphosphoric acids, P_2O_5, wt%		*Determined from the analysis results**	*Determination error*	
			Relative, %	*Mean square error*
Total content,	13.74	13.31	3.13	3.41
including:				
mono-	4.33	4.26	1.62	0.77
di-	3.14	3.00	4.46	0.93
tri-	2.47	2.41	2.43	0.51
tetra-	3.38	2.27	3.78	0.71
penta-.	1.42	1.37	3.52	0.37

* Average of five parallel determinations.

The results of the anionic composition analysis of the model mono- and polyphosphoric acid samples indicate that the application of paper chromatography with quantitative evaluation of each polymeric anion provides reliable and reproducible data.

To further identify the composition of the polyphosphoric acids, the ^{31}P NMR spectra were recorded using a *Bruker WP-80* spectrometer, following the methodology described in [7].

3. Results and Discussion

The results of evaluating the duration of the hydration process of the initial P_4O_{10} and the high–molecular–weight phosphoric acids formed as intermediate products of its degradation in an aqueous solution of monophosphoric acid are presented in Table 2.

According to the obtained data, an increase in the duration of hydration of the prepared polyphosphoric acid mixture leads to a gradual decrease in the number of distinct acids present in the composition. Specifically, in a mixture of polyphosphoric acids containing 65.0% total P_2O_5, eight different polyphosphoric acids were initially identified. Three hours after preparation, the mixture contained only six phosphoric acids instead of eight: $H_8P_6O_{19}$, $H_7P_5O_{16}$, $H_6P_4O_{13}$, $H_5P_3O_{10}$, $H_4P_2O_7$, and H_3PO_4. Nine hours later, the number of polyphosphoric acids in the mixture decreased to four. The final (and sole) product of hydration was identified as monophosphoric acid, H_3PO_4 (Table 2).

Table 2.

Dependence of the number of phosphorus atoms in the acids formed in the P_4O_{10}–H_2O system on the duration of degradation

Phosphorus concentration (calculated as total P_2O_5), %	Duration of P–O–P bond degradation, hours							*Equilibrium state of the P_4O_{10}–H_2O system*
	0.17	1.5	3.0	9.0	20.0	36.0	48.0	
65.0	8	7	6	4	3	1	1	1
70.6	8	7	6	5	4	3	2	2
75.1	9	8	8	7	5	4	3	3
77.0	9	8	7	6	5	4	4	4
78.5	≥9	8	8	7	6	6	5	5
80.5	≥9	≥8	8	8	7	7	6	7
82.7	≥9	≥9	≥9	≥9	9	8	9	9

Experimental data indicate that the hydration and degradation processes were completed within two days after the preparation of the mixture (Table 2). The maximum degree of polymerization of the phosphate anion observed in all experiments was found to be proportional to the total phosphorus content of the mixture.

According to the results of chromatographic studies, the composition of polyphosphoric acids with linear anion structures, in addition to low–molecular–weight species, includes relatively high–molecular–weight acids of compositions $H_8P_6O_{19}$, $H_9P_7O_{22}$, and $H_{10}P_8O_{25}$. The intense coloration observed in the region of the chromatogram close to the origin (τ = 0.1 and 1.5 h) indicates the presence in the freshly prepared mixture of unresolved condensed phosphoric acids containing more than 9–10 phosphorus atoms in the chain.

An increase in the total phosphorus concentration in the prepared mixture leads to a rise not only in the number of linear polyphosphoric acids but also in cyclic ones. For example, in a mixture with a total phosphorus concentration of 82.7% P_2O_5, cyclotri– and cyclotetraphosphoric acids were identified.

NMR spectroscopy of phosphoric acids of varying concentration revealed that almost all spectra contained three distinct signals. The signal located in the highest field was attributed to phosphorus atoms situated in the middle of the –P–O–P– chain. The signal recorded in the lowest field was assigned to phosphorus atoms of monophosphoric acid. The third signal was attributed to the phosphorus atoms of the terminal groups of the –P–O–P– polyphosphoric chain.

As the concentration of phosphoric acid increased from 72.4% total P_2O_5 to 85.0%, the intensity of the signal corresponding to phosphorus atoms of monophosphoric acid decreased almost to zero. Conversely, the intensity of the signal of phosphorus atoms of the middle groups increased from zero to a maximum value. The intensity of the signals from phosphorus atoms of the terminal groups initially increased, reached a maximum at 79.4% total P_2O_5, and then decreased with further increases in acid concentration.

Summarizing the experimental data obtained in the determination of the composition of condensed phosphoric acids formed during the hydration of P_4O_{10}, it can be concluded that the mechanism of this process is significantly more complex than that proposed by the authors [3–5].

The first and second stages of the interaction between P_4O_{10} and H_2O proceed sequentially with the initial formation of ultraphosphoric acid of composition $H_2P_4O_{11}$, which is subsequently converted into cyclotetraphosphoric acid, $H_4P_4O_{12}$. In this process, the original ring structure of phosphorus(V) oxide remains intact.

The destruction of the ring occurs at the third stage of the process, when cyclotetraphosphoric acid ($H_4P_4O_{12}$) is transformed into tetraphosphoric acid, $H_6P_4O_{13}$, possessing a linear anionic structure. According to our experimental data, the subsequent behaviour of tetraphosphoric acid is dual.

On one hand, it undergoes further hydration and degradation of the –P–O–P– bonds, simplifying its anionic composition:

$$H_6P_4O_{13} + H_2O = H_5P_3O_{10} + H_3PO_4 \quad (1)$$

$$H_5P_3O_{10} + H_2O = H_4P_2O_7 + H_3PO_4 \quad (2)$$

$$H_4P_2O_7 + H_2O = 2H_3PO_4 \quad (3)$$

On the other hand, tetraphosphoric acid participates in condensation reactions, leading to the formation of higher–polymer linear phosphoric acids, which can be schematically represented as:

$$5H_6P_4O_{13} = 4H_7P_5O_{16} + H_2O \quad (4)$$

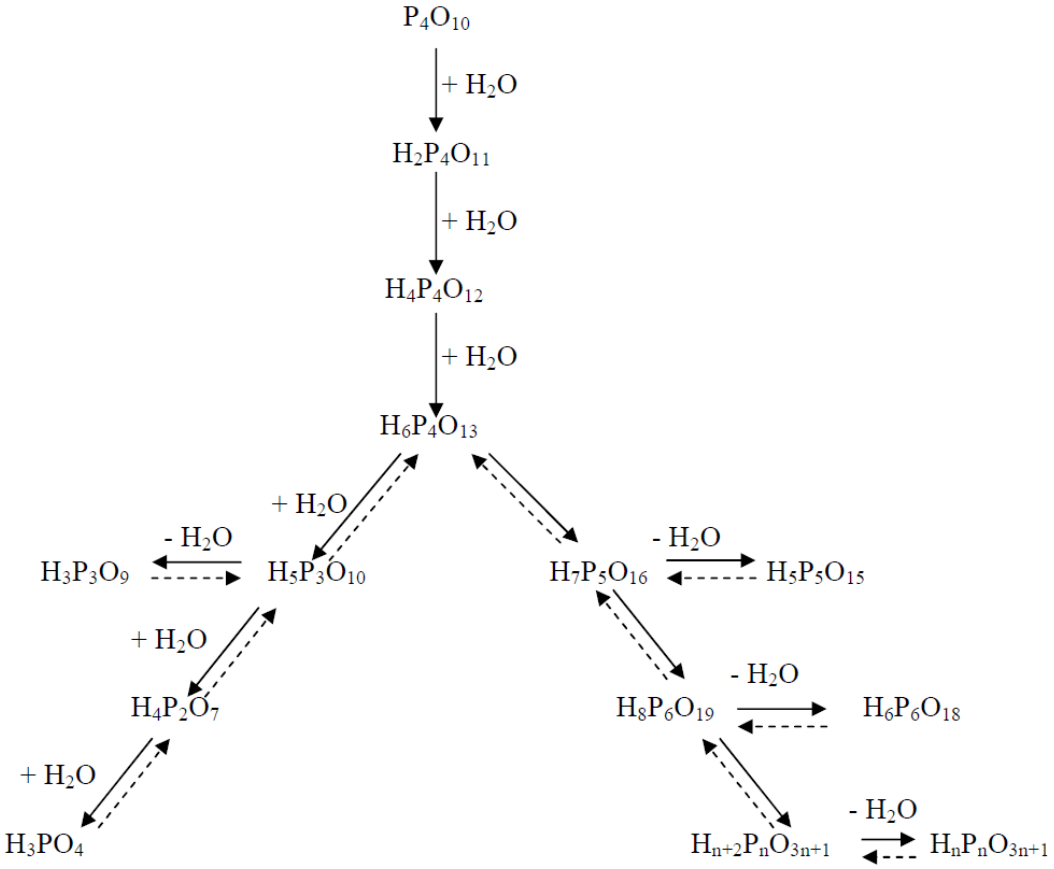
$$6H_7P_5O_{16} = 5H_8P_6O_{19} + H_2O \quad (5)$$

$$7H_8P_6O_{19} = 6H_9P_7O_{22} + H_2O \quad (6)$$

or, in general form:

$$(n+1)H_{n+2}P_nO_{3n+1} = nH_{n+3}P_{n+1}O_{3n+4} + H_2O \quad (7)$$

The sequence of the main stages of the interaction process in the phosphorus(V) oxide–water system can be represented by the following general scheme:



Thus, the formation of highpolymer linear phosphoric acids observed based on NMR and paper chromatography data in the initial stage of hydration of phosphorus(V) oxide is explained by the polycondensation of tetraphosphoric acid.

The existence of cyclic phosphoric acids in the P_4O_{10}–H_2O system has been described in [1] and is experimentally confirmed in the present work. Their formation from polyphosphoric acids with linear anion structures is most likely the result of dehydration of the latter. The cyclization of two terminal – PO_2H_2 groups of a linear acid leads to the formation of cyclic penta-, hexa-, and higher condensed acids according to the following scheme.

In other words, dehydration reactions of linear polyphosphoric acids result in the rearrangement of the linear anion into a cyclic structure:

$$H_5P_3O_{10} = H_3P_3O_9 + H_2O \quad (8)$$

$$H_6P_4O_{13} = H_4P_4O_{12} + H_2O \quad (9)$$

$$H_7P_5O_{16} = H_5P_5O_{15} + H_2O \quad (10)$$

$$H_{n+2}P_nO_{3n+1} = H_nP_nO_{3n} + H_2O \quad (11)$$

It should be noted that the likelihood of the formation of acids with a cyclic anion structure from linear polyphosphoric acids according to equations 8–11 depends on their composition. The longer the chain of the linear acid, the less probable the formation of cyclic acids due to steric hindrance in the approach of terminal groups of the linear acid.

In this regard, it should be considered that with an increase in the chain length of linear acids, the formation of not cyclic polyphosphoric acids but branched or conjugated isopolyphosphoric acids of the general formula becomes more probable $H_{nR}P_nO_{n(5+R)/2}$, where $R = H_2O/P_2O_5$.

Thus, the present study proposes for the first time an experimentally substantiated complete scheme of the real sequence of the main stages of phosphorus(V) oxide hydration. It has been shown that the duration of reaching the equilibrium state in the P_4O_{10}–H_2O system does not exceed 48 hours.

4. Conclusions

It has been experimentally confirmed that, depending on the phosphorus components in the P_4O_{10} – H_2O system, condensed phosphate acids with different anion structures occur – linear (with a degree of polycondensation n = 2–9) or cyclic (with n = 4).

For the first time, it has been substantiated that the direct precursor for the formation of linear polyphosphoric acids is cyclotetraphosphoric acid – an intermediate product of phosphorus(V) oxide hydration. The origin of condensed phosphoric acids with cyclic anion structures is secondary. They are formed as a result of the condensation of the corresponding polyphosphoric acids with linear anion structures.

It has been demonstrated that the duration of attaining equilibrium in the P_4O_{10}–H_2O system does not exceed 48 hours.

A modern scheme of the P_4O_{10} hydration process has been proposed.

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