# Kinetics of Acid-Catalyzed Hydrolysis of a Polyphosphate in Water

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The zeroth-order reaction of the hydrolysis of sodium polyphosphate in water at pH = 0 can be explained assuming the formation of a pentacovalent terminal phosphorus intermediate. A terminal unit is activated for hydrolysis by protonation of the double-bond oxygen on that unit followed by a nucleophilic attack of water. Proton transfer from an OH group to a P−O−P bond breaks the bond, thereby shortening the phosphate polymer. A mathematical equation is developed to explain the reaction order of the hydrolysis.

## Introduction

Sodium polyphosphate is an inorganic polymer consisting of $PO_4$ tetrahedra linked through oxygen atoms on the corners.[1] Quenching a phosphate melt results in a water-soluble glass that consists of polyphosphates. In water, polyphosphates are linear chains with an average length of 85 phosphate units. These polymers are not stable in acidic solutions, and they hydrolyze to orthophosphoric acid. Hydrolysis of a polyphosphate solution is catalyzed by the acidity of the medium. Decreasing the pH causes an increase in the rate of hydrolysis. In a previous paper it was shown that hydrolysis of a sodium polyphosphate at pH = 0 could be approximated by a zeroth-order reaction.[2] The reaction order is 0.09 in a concentration range of 1−3.3 $mol{\cdot}L^{-1}$. This is illustrated in Table 1. It is concluded that hydrolysis predominantly takes place at terminal phosphate units and that the energy of activation is 57 kJ/mol P−O−P bonds severed with a preexponential factor (Arrhenius plot) of $1.89 \times 10^5$ $mol^{-1}{\cdot}L^{-1}{\cdot}s^{-1}$ as determined experimentally by means of Raman spectroscopy.

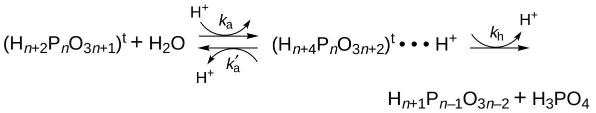
**TABLE 1: Rates of Hydrolysis of Sodium Polyphosphates ($\nu_{polyphosphate}$) Dissolved in Water at 22 °C and pH = 0**

| pH | initial phosphate unit concn ($mol{\cdot}L^{-1}$) | $\nu_{polyphosphate}$ ($mol{\cdot}L^{-1}{\cdot}h^{-1}$) |
|---|---|---|
| 0.0 | 3.3 | 0.052 |
| 0.0 | 1.7 | 0.048 |
| 0.0 | 1.1 | 0.047 |
| 0.0 | 0.7 | 0.038 |
| 0.25 | 3.2 | 0.029 |

## Kinetics

Since hydrolysis of a sodium polyphosphate solution at pH = 0 primarily takes place at terminal phosphate units, terminal and nonterminal units in this polymer will be considered separately in the following discussion. Instead of using a polymer concentration, concentration of phosphate units will be used, and it can be assumed that a direct relation exists between the polymer concentration and the terminal unit concentration.

Apparently, protonation of a polyphosphate is involved. A protonated polyphosphate is a kind of activated intermediate and/or leads to an intermediate that makes hydrolysis possible.



$$(H_{n+2}P_nO_{3n+1})^t + H_2O \underset{k'_a,\ H^+}{\overset{H^+,\ k_a}{\rightleftharpoons}} (H_{n+4}P_nO_{3n+2})^t \cdots H^+ \xrightarrow{k_h,\ H^+} H_{n+1}P_{n-1}O_{3n-2} + H_3PO_4 \quad (1)$$

$n$ is the number of phosphate units in a chain and has a theoretical minimum of two. $H_{n+2}P_nO_{3n+1}$ is the general formula of the polymers, and $[H_{n+2}P_nO_{3n+1}]$ its concentration. The relation between the two general formulas of the polyphosphate is the removal of one $HPO_3$ unit. Subtracting a $HPO_3$ unit from $H_{n+2}P_nO_{3n+1}$ results in the new general formula of the polymer. It is important to note that the extra superscript t in the formula or concentration represents the terminal phosphate units in the following discussion. Also note that the polymer is activated only when terminal phosphate units are protonated and that $(H_{n+4}P_nO_{3n+2})^t$ is the intermediate. The intermediate could react back to the reactants or be hydrolyzed to form the products. $k_a$ is the reaction constant for the formation of the intermediate, while $k'_a$ refers to the backward reaction. $k_h$ correspond to the actual hydrolysis. At this stage nothing can be said about the structure of the intermediate. The above consecutive reaction suggests a preequilibrium between the reactants and the intermediate if the concentrations of the intermediate and the terminal phosphate units remain constant. Under steady-state conditions the intermediate concentration must be constant. If a terminal phosphate unit is being hydrolyzed, a new terminal unit is formed keeping the concentration of these units also constant.

The rate of hydrolysis could be written as

$$\frac{\delta\,[H_{n+2}P_nO_{3n+1}]}{dt} = k_h{\cdot}[(H_{n+4}P_nO_{3n+2})^t] \qquad (2)$$

Applying steady-state conditions for the intermediate, it is possible to relate the concentration of the intermediate to the $k$ values in eq 1. Water in the reaction can be considered as a constant because it is the medium of the hydrolysis.

$$\frac{\delta[(H_{n+4}P_nO_{3n+2})^t]}{\delta t} = k_a{\cdot}[H^+][(H_{n+2}P_nO_{3n+1})^t] - k'_a{\cdot}[(H_{n+4}P_nO_{3n+2})^t] - k_h{\cdot}[(H_{n+4}P_nO_{3n+2})^t] = 0 \quad (3)$$

Solving the equation gives

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$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a}{(k_h + k'_a)} \cdot [H^+][(H_{n+2}P_nO_{3n+1})^t] \quad (4)$$

A polymer is activated for hydrolysis after protonation. Besides terminal phosphate units, nonterminal phosphate units could also be protonated. The total concentration of protons used, defined as $H_0^+$, is the concentration of $H^+$ and the concentration of protonated phosphate units, distinguishing between terminal (t) and nonterminal (nt) units:

$$[H_0^+] = [H^+] + [(H_{n+4}P_nO_{3n+2})^t] + [(H_{n+4}P_nO_{3n+2})^{nt}] \quad (5)$$

Now eq 4 can be rewritten as

$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a}{(k_h + k'_a)} \cdot ([H_0^+] - [(H_{n+4}P_nO_{3n+2})^t] - [(H_{n+4}P_nO_{3n+2})^{nt}]) \cdot [(H_{n+2}P_nO_{3n+1})^t] \quad (6)$$

which rearranges to

$$[(H_{n+4}P_nO_{3n+2})^t] = \frac{k_a([H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}]) \cdot [(H_{n+2}P_nO_{3n+1})^t]}{k_h + k'_a + k_a[(H_{n+2}P_nO_{3n+1})^t]} \quad (7)$$

Combining eqs 2 and 7 results in a new formulation for the hydrolysis of a polyphosphate

$$\frac{\delta[H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot [(H_{n+4}P_nO_{3n+2})^t] = \frac{k_h \cdot ([H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}])[(H_{n+2}P_nO_{3n+1})^t]}{K_m + [(H_{n+2}P_nO_{3n+1})^t]} \quad (8)$$

where

$$K_m = \frac{k_h + k'_a}{k_a}$$

Equation 5 can be written in the following form: $[H_0^+] - [(H_{n+4}P_nO_{3n+2})^{nt}] = [H^+] + [(H_{n+4}P_nO_{3n+2})^t]$. The left-hand side is present in eq 8. On the right-hand side, $H^+$ is constant at a constant pH. Under steady-state conditions the concentration of the intermediate remains constant. Since the concentration of terminal phosphate units is also constant, the whole left-hand side must be constant. Substituting this side in eq 8 results in an extra constant, which will be defined as $k_p$:

$$\frac{\delta[H_{n+2}P_nO_{3n+1}]}{\delta t} = k_h \cdot k_p \cdot \frac{[(H_{n+2}P_nO_{3n+1})^t]}{K_m + [(H_{n+2}P_nO_{3n+1})^t]} \quad (9)$$

When $[(H_{n+2}P_nO_{3n+1})^t] \gg K_m$, eq 9 reduces to $\delta[H_{n+2}P_nO_{3n+1}]/\delta t = k_h \cdot k_p$, which is initially zeroth-order. The concentration range of the polyphosphate samples in which zeroth-order is observed ranges from 0.8 to 3.6 mol phosphate units/L. If the average chain length of a polymer is 85, the concentration of terminal phosphate units ranges from 0.019 to 0.085 mol/L. $k_p$ depends on the concentration of the intermediate and therefore slightly on the polyphosphate concentration accounting for the small increase in the rate of hydrolysis with concentration. This dependency, however, is negligibly low.

Equation 9 explains the approximate zeroth-order behavior at high polymer concentrations ($1-3.3$ mol·L$^{-1}$·h$^{-1}$). It also explains the behavior at lower concentrations. As the polyphosphate concentration is low, the number of terminal phosphate units is also low. $K_m$ cannot be neglected anymore, and the rate of hydrolysis depends on both the pH and the polymer concentration. This results in a lower rate of hydrolysis.

The equation also explains the shape of the hydrolysis curve. A polyphosphate solution has a distribution of chain lengths. During hydrolysis, polymers are shortened, but the rate is constant as long as the number of terminal phosphate units remains constant. Once a chain is completely hydrolyzed, the terminal units of the chain are destroyed. Short units are completely hydrolyzed in a shorter time and the concentration of terminal units decreases, affecting the rate of hydrolysis. As a consequence, the polyphosphate curve levels off, and a plateau is reached when all polymers are completely hydrolyzed.

## Mechanism

Strauss et al. studied hydrolysis of branched sodium polyphosphate solutions.[3] They found a first-order dependence based on viscosity measurements. Ray also mentioned first-order hydrolytic degradation with an activation energy of 104 ± 8 kJ/mol determined by viscosity measurements in a temperature range of 25−90 °C.[4]

The order seems to contrast the results obtained by Raman spectroscopy, but the two processes are of a different nature. Strauss et al. and Ray studied hydrolysis of branched polymer solutions. The P−O−P bonds at branch points are much weaker compared to nonbranched bonds. The former bond type hydrolyzes first. As a consequence the viscosity decreases accordingly. When this type of hydrolysis is completed, linear chains are present in solution,[5] and this is the starting solution of the acid-catalyzed hydrolysis studied in this paper. Before the pH was lowered, the neutral polyphosphate solution had been standing for 24 h to ensure that all branched points were hydrolyzed. In this way hydrolysis of these points does not interfere with the hydrolysis process in acidic medium.

Ray presented an enthalpy expressed in kilojoules per mole of P−O−P bonds severed implying that all these bonds are identical, which is in practice not the case. P−O−P bonds at branches hydrolyze in neutral solutions, but the remaining bonds stay intact indicating that the latter are more stable. Therefore, the energy of activation for the hydrolysis of nonbranched P−O−P bonds in neutral solutions should be higher than 104 kJ/mol. The activation energy of acid-catalyzed hydrolysis is 57 kJ/mol.

Before a polyphosphate is to be hydrolyzed, it must be made susceptible to nucleophilic attack of water first. In neutral solutions this can be accomplished by the resonance structure of a phosphate unit, which could be interpreted as the transition state. In acidic solutions protonation of the double-bond oxygen on the terminal phosphate unit in a polymer also activates the polymer for nucleophilic attack of water. In this case a hydrated species represents the transition state. Protonation/deprotonation is instantaneous, but the nucleophilic attack of water to form the intermediate is a kinetic step in the process

The pathway in which terminal phosphate units are activated by protonation has a lower activation energy compared to the noncatalyzed pathway. This is exactly the function of a catalyst. It does not change the thermodynamic states of the reactants and intermediate, but it lowers the activation energy. It must be noted that the hydrolysis of branched points in a polymer does not necessarily follow the mechanism in eq 10. The value of its activation energy is used and extrapolated to the reaction profile in the case of the hydrolysis of terminal phosphate units in neutral solutions. After nucleophilic attack, constitutional water is added to the terminal phosphate unit in both processes

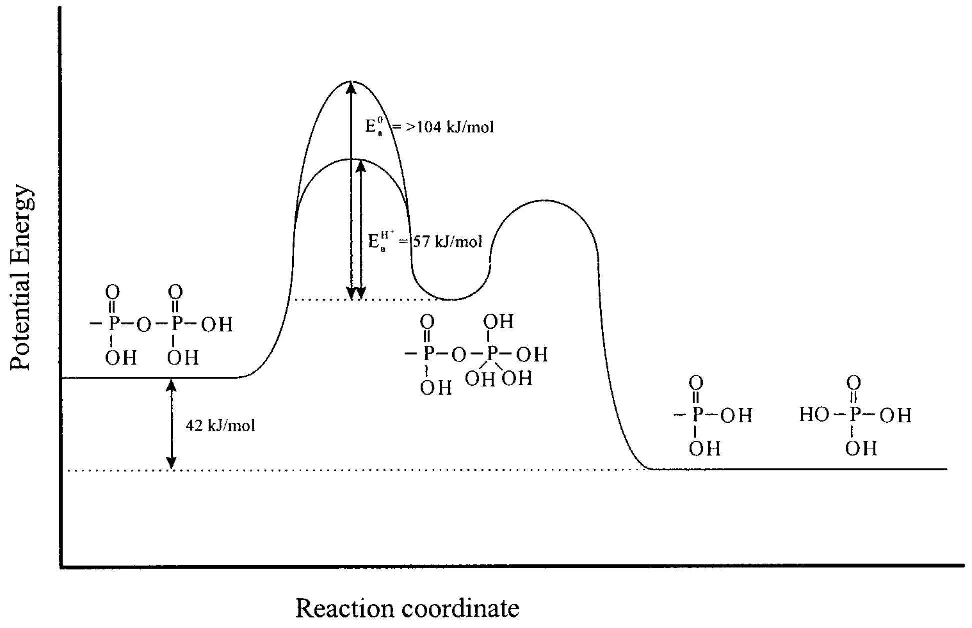
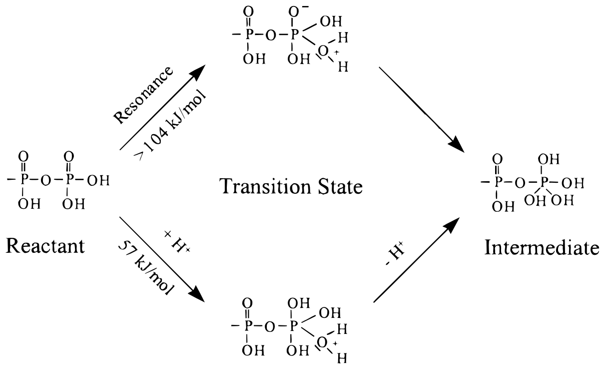


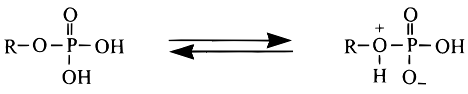
**Figure 1.** Reaction energy diagram of the hydrolysis of a sodium polyphosphate solution with and without an acid catalyst.

resulting in a five-coordinated terminal phosphorus atom. According to the literature the mechanism of the hydrolysis of diesters also involves a five-coordination of phosphorus by oxygen atoms.[6−8] Lowering the activation energy results in a higher concentration of intermediate, and by recalling eq 2 it can be seen that this leads to an increase in the rate of hydrolysis.



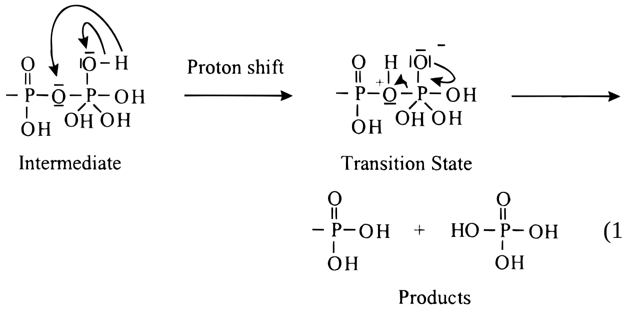
(10)

From the intermediate onward, the reaction profiles of acid-catalyzed and noncatalyzed hydrolysis are the same. The polyphosphate structure in the second transition state in the reaction energy diagram is not well-known. If the hydrolysis is analogous to acid-catalyzed hydrolysis of esters, transfer of a proton from one oxygen to another is involved to break a P−O−P bond.[9] Proton transfer is not uncommon in phosphates. It occurs in sodium phosphor amidate ($NaHPO_3NH_2$) and acid monoesters of phosphates.[10] The formula of the former compound differs slightly from sodium dihydrogen phosphate. An oxygen is replaced by an amino group and one hydrogen is removed to balance the charge. More important are proton shifts in acid monoesters. These types of phosphates have a very close resemblance to phosphate polymers. The oxygen in the P−O−R bond is protonated by an OH group of an adjacent terminal phosphate group resulting in a sort of zwitterion (eq 11).



$$R-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH \rightleftharpoons R-\overset{+}{\underset{\underset{H}{|}}{O}}-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-OH \quad (11)$$

If R represents the rest of a polyphosphate, the bond-breaking process can be explained in terms of proton transfer. On this basis the second part of the hydrolysis could be explained as follows:



(12)

There is no difference in protonating a terminal or a nonterminal phosphate, but hydrolysis takes place at the terminal phosphate after protonation of the double-bond oxygen. Proton transfer from a terminal phosphate unit might be easier because of the presence of four OH groups instead of two in a nonterminal unit. Compare the difference in acidity between orthophosphoric acid, monobasic phosphate, and dibasic phosphate. The acid form with three OH groups is a better proton donor ($pK_a = 2.1$) than monobasic phosphate ($pK_a = 7.2$) with two groups or dibasic phosphate ($pK_a = 12.3$) with one OH group.[11] Inductive stabilization of a negatively charged oxygen in a terminal phosphate unit is expected to be higher as in a nonterminal unit. Chandler and Kirby[6] accepted the idea that the hydrolysis proceeds by way of a pentacovalent intermediate in which a neighboring nucleophilic OH group could act as a general acid and/or base depending on their $pK_a$. They also reported that the breakdown of a pentacovalent intermediate should be rapid and its formation rate-determining. This is in line with the mechanism presented here. Formation of an intermediate in the hydrolysis of a polyphosphate is an assumption made to explain the order of the reaction. Furthermore, if the rate of formation is rate-determining and the actual breakdown is rapid, the measured activation energy determined in this paper is confined to the first step of the hydrolysis, and the activation energy for the second step must be much lower.

The height of the second transition state is not important because it remains the same in both processes.

In addition, steric hindrance could also play a role. In the intermediate the relevant phosphorus atom is 5-fold coordinated. If a nonterminal unit is protonated, two groups form the rest of the polymer and can be regarded as bulky ligands inhibiting the large coordination number of the intermediate. Steric hindrance increases the barrier of the transition state, reducing the rate constant of the hydrolysis. A reaction energy diagram could now be constructed and is shown in Figure 1.

The rate of hydrolysis does not depend only on the activation energy. According to the Arrhenius equation, a preexponential factor is also involved. Hydrolysis at a higher pH is slower. In a polyphosphate solution with a pH of 0.25, the reaction constant of the hydrolysis is 0.029 $\text{mol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$. Since the reaction energy diagram remains the same because it is based on thermodynamic properties, the preexponential factor must be lower. Using a single-point determination, the preexponential factor is $9.9 \times 10^4$ $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ at a temperature of 22 °C. Strauss et al. found a reaction coefficient of 0.5 $\text{h}^{-1}$ for the hydrolysis of branched P−O−P bonds at 25 °C. Combining this with the activation energy given by Ray results in a preexponential factor of $2.2 \times 10^{14}$ $\text{s}^{-1}$, which is appreciably higher compared to the factor in acid-catalyzed hydrolysis ($1.89 \times 10^5$ $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$). The preexponential factor of acid-catalyzed hydrolysis decreases with an increasing pH, but in the noncatalyzed process, which is in neutral solutions, it is much higher. This can be explained as follow. A preexponential factor in acid-catalyzed hydrolysis involves collisions between three types of particles i.e., a polyphosphate, $H^+$ and $H_2O$. As the pH increases, the concentration of $H^+$ decreases, lowering the chance of a collision between the three participating particles simultaneously. The pH dependence could be seen in eq 9 since $k_p$ is related to the concentration of $H^+$. In nonacid-catalyzed hydrolysis only two reactants are involved and the chance of a collision between two particles is much higher, reflected in the corresponding preexponential factor.

## Concluding Remarks

Polyphosphates in neutral solutions are stable. Hydrolysis is catalyzed by $H^+$ and shows initially an approximate zeroth-order behavior. A mathematical expression for the rate of hydrolysis explaining zeroth-order behavior can be developed assuming an intermediate is involved in the process. Hydrolysis is mainly limited to terminal phosphate units.

The literature stated that the rate of hydrolysis is determined by concentration.[1,3,4] This is the case for noncatalyzed hydrolysis, but not for an acid-catalyzed reaction.

Stability of linear polyphosphate in neutral solutions can be explained in terms of activation energies using the activation energy for the hydrolysis of branched phosphate units.

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