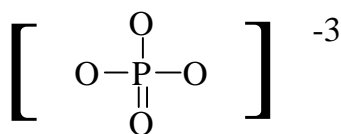


The Hydrolysis of Pyrophosphate

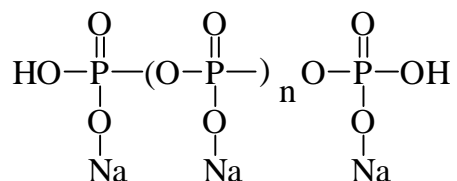
Introduction

Large amounts of phosphorous compounds used in detergents, animal feeds, fertilizers, water softener and anti-corrosive treatments, surface treatments, plasticizers, gasoline additives, and insecticides are disposed of using water. Many of these compounds fall into the category of phosphates - a diverse classification itself but characterized by P-O bonds in which the phosphorus is in the +5 state. Orthophosphates are those forms which include the $(\text{PO}_4)^{-3}$ species itself. Polyphosphates are chains of orthophosphate (with variable chain lengths) such as the naturally occurring sodium hexametaphosphate. There are even cyclic metaphosphates with ring structures.

Orthophosphate



Sodium Hexametaphosphate



Since many phosphates wind up in water (and some are even added to municipal water to prevent corrosion), it is important to understand the hydrolysis of these species. The hydrolysis of almost all inorganic phosphates proceeds eventually to orthophosphate, but there can be many intermediate breakdown products, especially for long chain polyphosphates. Identification of these breakdown products can be difficult. Several colorimetric methods are based on the formation of a yellow molybdenum complex with orthophosphate followed by a reduction (with ascorbic acid for example) to an intense blue colored complex. To determine the concentration of polyphosphate two samples must be analyzed. One sample must be entirely converted to the ortho form and analyzed; the second sample is analyzed directly for the ortho form. The poly concentration is determined indirectly by subtraction. Ion chromatography is an excellent method for detecting intermediates but is tedious and time consuming. Further the instrumentation is not often available in the research laboratory.

Phosphorus 31 NMR is another good technique for following the hydrolysis of polyphosphates. In general three types of phosphorus atoms are present in polyphosphates and their degradation products which give rise to three peaks: the ortho P itself, P atoms that are at the ends of polyphosphate chains (terminal P atoms), and P atoms that are in the interior of long chains. It is interesting that for the most part the chemical shift values of all the interior P atoms is fairly constant for a particular polyphosphate and can be usually grouped together. The usual P^{31} spectrum for an aqueous polyphosphate solution thus contains two peaks at the beginning. Soon an ortho peak appears as the hydrolysis progresses. Integration of the peaks gives area values that can be used to follow quantitatively the hydrolysis.

Our task in this lab is to follow the hydrolysis of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$). To accomplish an experiment within the time frame of our lab period, we will choose acid conditions which will accelerate the hydrolysis. The area of the unhydrolyzed phosphorus peak will be followed over the course of the lab period by taking spectra every hour if possible, and a determination of the rate law and specific rate constant for the reaction will be determined by fitting to an integrated kinetic rate law in the usual way.

Procedure

30. mg of sodium pyrophosphate is dissolved in 1 mL of D_2O . DNO_3 is added dropwise until the pH is about 1. A NMR sample tube is filled and spectra are taken over at least an 8 hour period. Additional spectra may be taken the next day. Each FID should be saved on the hard drive using the following code: RR07PY##.pH. The ## designation numbers the spectra: 01, 02, etc. pH should be a 3 digit number for the pH value, example pH 1.23 would be 123.

An external reference tube is used to normalize the peak areas. The external reference is an orthophosphate solution that is at a pH of 9.73 so as not to interfere with the ortho peak from the hydrolysis. The external reference tube is inserted inside the sample NMR tube.

Phosphorus NMR comments

If you have used the NMR with Dr. Matthews his instructions are excellent and very detailed. There are only a couple of changes from a proton or C13 job to a P^{31} job.

- In the beginning before or after inserting the sample press #3 to use the P^{31} probe.
- Although we will be setting the chemical shifts using the external standard peak in PC NMR, a rough chemical shift will be obtained at the console using the setup file and the EP function. After shimming (using z and z^2) type "RJ PFA", press enter, then type "PJ PFA", press enter. This sets the chemical shift at zero to be the P peak found in 85% phosphoric acid. The reason your ortho peaks will not be exactly at zero is due to the pH of the sample and external standard solutions.
- 64 scans will give you a nice spectrum.

Data Analysis

Transfer each FID from the Bruker hard drive to the lab computer and copy to a disk or flash drive. Open the file in an NMR program such as we have from ACD. Do a Fourier transform on each spectrum and integrate the peaks. Set the ortho peak of the external standard (the peak at the most positive chemical shift value) to 4.5 ppm and normalize to it. Use the area of the terminal peak (about -9.5 ppm) as being proportional to the pyrophosphate concentration. Graph:

0 order	pyrophosphate concentration vs time
1 st order	ln (pyrophosphate concentration) vs time
2 nd order	1/(pyrophosphate concentration) vs time

Determine the best model and then find the specific rate constant from the slope. Compare with the literature value for 6N HCl given in the reference below.

Reference

M. Kawabe, O. Ohaski, et. al., Phosphorus Nuclear Magnetic Resonance in Polyphosphates and Determination of Their Hydrolysis Rate Constants, *Bulletin of the Chemical Society of Japan*, 43, 3705-3710 (1970) [There is a copy in the chem library - we do not carry this journal]

The Short Report (follow this format)

1. Print the integrated Fourier transforms of each spectrum as determined above with annotations for reference, ortho, and pyro as well as pH and time. Make sure the peak areas are shown on the spectra.
2. Make a data table of time, ortho area, and pyro area.
3. Submit the proper graphs to prove whether the order of the reaction is 0, 1st, or 2nd order.
3. Find the rate constant for the reaction.
4. Compare to other values for similar rate constants found in the C wing hallway bulletin board and in the reference above (Kawabe).