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Phosphorus Nuclear Magnetic Resonance in Polyphosphates and Determination of Their Hydrolysis Rate Constants

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The phosphorus nuclear magnetic resonance spectra of several condensed phosphates (polyphosphates) were measured in aqueous solutions. The NMR spectra generally consist of three peaks which correspond to the phosphorus atoms at the end and middle of the molecular chain and in orthophosphoric acid which is the final product of the hydrolysis. The chemical shift and, for some phosphates, spin-spin coupling constants were obtained. Both depend on pH of the solution. The chemical shifts for the end and middle phosphorus atoms depend also on the chain length of the molecule. The hydrolysis process of the phosphates can be traced by the observation of the time dependence of spectral line intensities. From this observation the rate constant of the hydrolysis is obtained for several phosphates. The values are comparable with those obtained by other methods.

The chain of –P–O–P– in polyphosphoric acid or polyphosphates molecule has been known to degrade by hydrolysis in aqueous solutions.[1–11] The degradation results in shorter chain molecules and finally in orthophosphoric acid. The rate of the hydrolysis is very slow at ordinary temperature and in neutral aqueous solution. Some of the polyphosphates have long half-life up to several years under such conditions.[8,9]

Phosphorus nuclear magnetic resonance is a useful method for the study of phosphates and related compounds. Several papers on this subject appeared in the past decade.[11–16] The reported studies so far, however, concern with the phosphorus compounds in their "static" state. This work deals with the "dynamical" process of the phosphorus compounds by nuclear magnetic resonance, that is, the hydrolysis process of polyphosphoric acids and polyphosphates.

The slow rate process of hydrolysis of the compounds enables us to study it by observing the

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increase or decrease of the intensity of phosphorus nuclear magnetic resonance signals as the hydrolysis process is going on. Rate constants were determined for several compounds from the data of the time dependence of the intensity, and assignment of the signals was made. The chemical shift and, in some cases, the magnitude of the spin-spin coupling constants were obtained.

Experimental

The compounds studied are shown in Table 1, with their structural formulas. Compounds Nos. 1,2,3,7,11 and 12 were commercial products, and Nos. 4,5,6,8,9 and 10 were synthesized.

Samples were dissolved in hydrochloric acid (0.5, 1, 3 and 6N), water, calcium chloride (3N) and sodium hydroxide (0.5, 1 and 12N). Concentration of the compounds was small because of their poor solubility. Saturated solutions (2—3 g in 10 m*l*) were used in most cases. The pH of solutions was measured with a pH meter.

Some compounds evolve a large amount of heat when dissolved and the temperature of the solutions is 90—110°C immediately after the dissolution. The temperature, however, decreases in several minutes to around 60°C. The effect of the heat evolution was taken into account for the analysis of data.

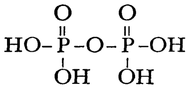
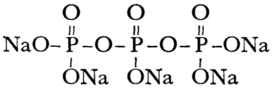
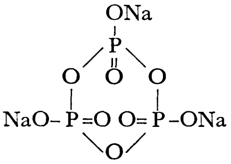
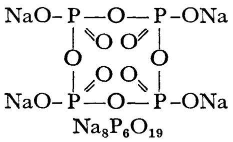
The NMR spectrometers used were Varian DP-60 and HR-60 operated at 15.1 MHz. The sample tube was 15 mm in outer diameter. The external reference for the chemical shift measurements was 85% orthophosphoric acid sealed in a glass tube 5 mm in outer diameter. The value of the chemical shift with respect to the orthophosphoric acid was determined by the usual sideband method. For the sample with fast rate of hydrolysis, the reference was the signal of orthophosphoric acid produced in the sample itself.

The relative amount of phosphorus atoms with different chemical environments in the course of hydrolysis was determined by measuring the height of the signals. Assignment of the signals to the phosphorus chemical species involved was made according to the fact that the phosphorus NMR signals of polyphosphates are classified into three groups.[11,13] They are signals M,E and O, and are the resonance lines of phosphorus atoms at the middle and end of –P–O–P– chain in a molecule and of the atom in orthophosphoric acid, respectively. In the spectrum, signal M appears at the highest field, signal E next and signal O at the lowest. The behavior of the signal intensity was in line with generally accepted hydrolysis process.[6—10] The spin-spin interaction splitting of the signal also supported the assignment.

Results and Discussion

NMR Spectrum. Polyphosphates in aqueous solution generally give three peaks which can be assigned to signals M (middle), E (end) and O

Table 1. Phosphorus compounds studied

1.	Pyrophosphoric acid	 $HO-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-OH$
2.	Na-Pyrophosphate	$Na_4P_2O_7$
3.	Na-Tripolyphosphate	 $NaO-\overset{O}{\underset{ONa}{P}}-O-\overset{O}{\underset{ONa}{P}}-O-\overset{O}{\underset{ONa}{P}}-ONa$
4.	Na-Trimetaphosphate	
5.	Na-Tetrametaphosphate	
6.	Na-Hexapolyphosphate	$Na_8P_6O_{19}$
7.	Na-Hexametaphosphate[a]	$(NaPO_3)_n$, $n=20$?
8.	Na-Icosapolyphosphate	$Na_{22}P_{20}O_{61}$
9.	Na-Polyphosphate ($\bar{n}=40$)[b]	$Na_{\bar{n}+2}P_{\bar{n}}O_{3\bar{n}+1}$
10.	Na-Polyphosphate ($\bar{n}=80$)[b]	$Na_{\bar{n}+2}P_{\bar{n}}O_{3\bar{n}+1}$
11.	Polyphosphoric acid	Mixture, linear.
12.	Na-Metaphosphate	$(NaPO_3)_n$

a) Commercial name.

b) $\bar{n}$ is the average chain length for the mixture of linear molecules with various chain lengths, counted by the number of phosphorus atoms in the chain.

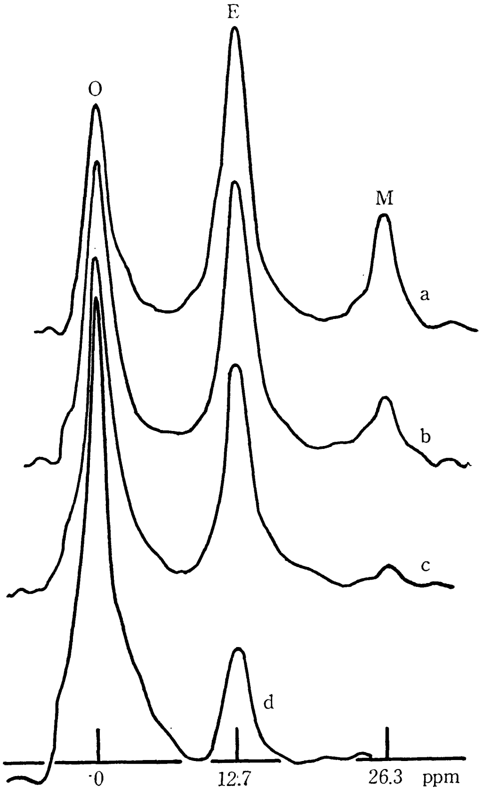


Fig. 1. NMR spectra of polyphosphoric acid in aqueous solution at different times after the dissolution of compounds. Spectra a, b, c and d correspond to 3, 9, 25 and 89 min, respectively.

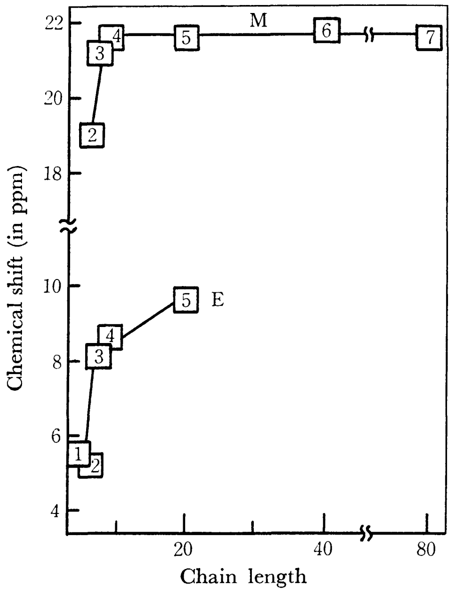


Fig. 2. Chemical shifts of M and E phosphorus atoms of the Na-phosphates with different chain length, refer to the phosphorus resonance in orthophosphoric acid. 1. Na-pyro-; 2. Na-tripoly-; 3. Na-tetrapoly-; 4. Na-hexapoly-; 5. Na-icosapoly; 6. Na-poly- ($\bar{n}=40$), 7. Na-poly- ($\bar{n}=80$), phosphates.

(ortho). A spectrum of polyphosphoric acid in aqueous solution is shown in Fig. 1 as a typical example. The time after dissolution is indicated. The heights of the signals vary with time. Each signal can be assigned unequivocally to M, E or O species. The chemical shifts for these species were measured.

Chemical Shift. The chemical shift of peaks M and E varies with the increase of the chain length of molecule as shown in Fig. 2. (The chemical shift of peak O referring to the external reference seems to be very small and can not be measured due to relatively poor resolution of the spectra.) The chemical shifts of species M and E increase for the compounds of short chain lengths up to $n=6$, where n is the number of phosphorus atoms in a chain of a molecule. In this range the chemical shift clearly depends on the chain length. However, the shifts for $n>6$ are almost constant. This suggests that in a long chain molecule most phosphorus nuclei are not much affected by their position in the molecule. The phosphorus nucleus at the boundary position between normal E and M species is expected to be sensitive to the change of position in a chain. However, for a long chain molecule the contribution of this kind of species to the whole signal intensity is very small, and its signal seems to lie at the skirt of signal M with very weak intensity and is not observed separately.

The chemical shift for compounds studied also depends on pH of the solution as shown in Fig. 3.

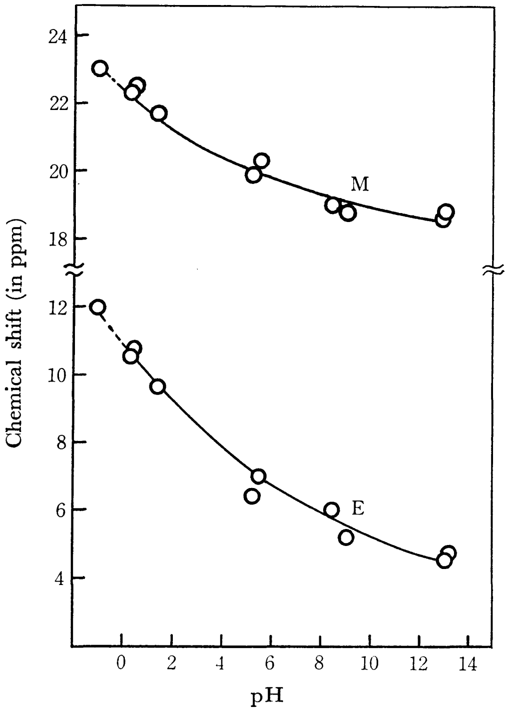


Fig. 3. pH Dependence of the chemical shift of Na-tripolyphosphate.

The signals do not cross (in the chemical shift scale) in the pH range observed. This shows that at any pH unique assignment of the signals can be made in the order of the field strength.

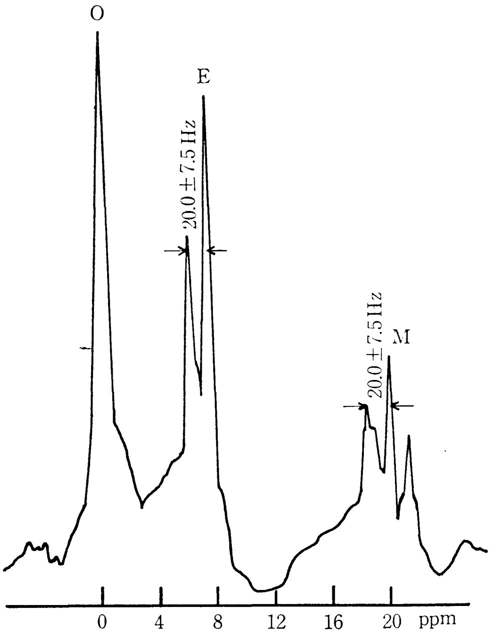


Fig. 4. Phosphorus NMR spectrum of Na-tripolyphosphate in 1N HCl solution.

Spin-spin Coupling. Sodium tripolyphosphate in solutions with pH 5, 9 and 13 gives spectra with splittings due to spin-spin coupling. This is the only case in which the spin-spin interaction splitting was observed. The splitting of the peaks are doublet and triplet as shown in Fig. 4. The magnitude of the splitting is around 20 Hz. This indicates that the coupling is between neighboring phosphorus atoms in the molecular chain.[13-15] The splitting gives a concrete assignment of the signals; the doublet at the low field side is due to species E and the triplet at the high field is due to species M.

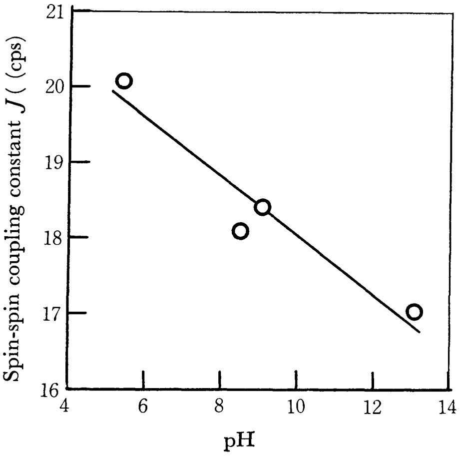


Fig. 5. pH Dependence of the spin-spin coupling constant of Na-tripolyphosphate.

The pH dependence of the coupling constant is evident for this compound as shown in Fig. 5. The coupling constant decreases from 20 to 17 Hz as pH increases from 4 to 13. This is in contrast to that by Crutchfield *et al.*[13)]

Analysis of Hydrolysis. The time variation of the NMR signal height is plotted in Figs. 6 and 7. Apparent variations of the spectra are summarized in Table 2.

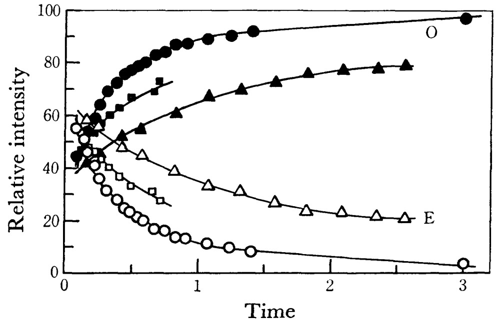


Fig. 6. Variation of the peak height (normalized to 100%) of phosphorus NMR spectral lines for species E and O in pyrophosphate molecules.
○, ●: $6\,\text{N}$ HCl solution; □, ■: aqueous solution; △, ▲: $3\,\text{N}$ $CaCl_2$ solution.

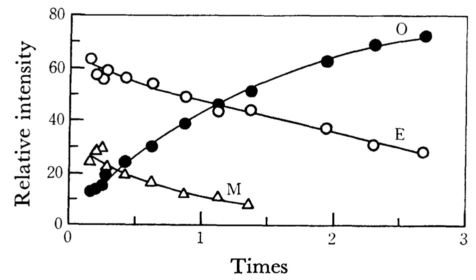


Fig. 7. Variation of the peak height (normalized to 100%) of phosphorus NMR spectral lines for species E, M and O in tripolyphosphate molecule ($6\,\text{N}$ HCl solution).

TABLE 2. APPARENT BEHAVIORS OF THE NMR SPECTRUM

Compound in soln.	Obsd. period	Variation of peaks			% of O at final obs.
		O	E	M	
Pyrophosphoric acid					
$6\,\text{N}$ HCl	3 hr	I.	D.	—	96%
aq.	1 hr	I.	D.	—	80%
$3\,\text{N}$ $CaCl_2$	4 hr	I.	D.	—	83%
$6\,\text{N}$ NaOH	96 hr	I.	D.	—	96%
Na-Tripolyphosphate					
$6\,\text{N}$ HCl	3 hr	I.	D.	D.	72%
aq. (pH 8.5)	24 hr	slightly			9%
Polyphosphoric acid					
$6\,\text{N}$ HCl	2.5 hr	I.	D.	D.[a)]	94%
aq.	1.5 hr	I.	D.	D.[b)]	84%
$6\,\text{N}$ NaOH	4 hr[c)]	I.	D.	D.	65%
Na-Tetrametaphosphate					
aq. (pH 6.0)	9 day	almost no			9%
Na-Metaphosphate					
$6\,\text{N}$ HCl	2 hr	I.	I-D.[d)]	D.	80%
aq. (pH 5.7)	9 day	almost no			5%

I.: Intensity increasing; D.: Intensity decreasing.
a) disappeared in 15 min.
b) disappeared in 1 hr.
c) reached equilibrium in 1 hr.
d) initially increased then decreased.

Basic assumptions for the treatment of the time dependence of the NMR signal intensity are as follows:

i) Hydrolysis of polyphosphoric acid or polyphosphate produces shorter chain compounds. The final product in the process is orthophosphoric acid.

ii) The phosphorus NMR spectra of original compounds and intermediates of the hydrolysis process consist of three peaks due to species M, E and O.

iii) In the course of hydrolysis, the chain degradation proceeds as a first order reaction process[2-9)], and the rate equation is

$$-\frac{d[\text{polyphosphate}]}{dt} = k[\text{polyphosphate}]$$

where k is the first order reaction rate constant.

iv) The peak height of the NMR signal is proportional to the amount of the phosphorus atoms in question.

Three unit degradation processes can be considered:

Process-1; the scission of E and M,

$$\text{-M-E} \longrightarrow \text{-E} + \text{O}.$$

Process-2; the scission of two M's,

$$\text{-M-M-} \longrightarrow \text{-E} + \text{-E}.$$

Process-3; the scission of two E's,

$$\text{E-E} \longrightarrow \text{O} + \text{O}.$$

If the original molecule is a linear chain, the initial numbers of the phosphorus species in a molecule are $(n-2)$ and 2 for M and E respectively, and if the molecule is in a ring form the number is n for M, where n is the number of phosphorus atoms in the original molecule. In the final stage of hydrolysis, the numbers of the species corresponding to one original molecule should be n for O and 0 for M and E when hydrolysis is completed. In principle, the relative amount of each species may be estimated at any intermediate stage of the degradation through processes 1, 2 and 3. For long chain molecules, however, there are many possibilities for the position of the chain scission in the degradation process. It is almost impossible to determine the relative amount of each species without knowing the rate of each degradation process. Thus, significant rate constants are obtained only for relatively simple systems such as pyrophosphate and tripolyphosphate.

Determination of the Rate Constant of Hydrolysis. *Pyrophosphoric Acid.* Pyrophosphoric acid has the simplest structure of the compounds studied. It undergoes hydrolysis to give orthophosphoric acid in one step by Process-3 as follows.

$$\text{P-O-P} \xrightarrow{k_3} 2\text{P}$$

Let us assume a first order reaction for the degradation. Then the rate of the hydrolysis is determined by the equation

$$\frac{dx}{dt} = k_3(a-x), \text{ or } \ln\frac{(a-x_1)}{(a-x_2)} = k_3(t_2-t_1),$$

where a is the initial quantity of the pyrophosphoric acid or the peak height of the NMR signal (species E). Therefore $(a-x_1)$ is the quantity at $t=t_1$ and k_3 is the rate constant (for Process-3).

Figure 8 shows the plot of $\ln[(a-x_1)/(a-x_2)]$ *vs.* (t_2-t_1) for pyrophosphoric acid. The plot gives a fairly straight line for a certain interval of time, and shows that the reaction is almost of the first order in the interval. The plot consists of two parts of straight lines. This is interpreted as follows: Phosphoric acid evolves a large amount of heat when dissolved in water. It is reasonable to consider that the heat accelerates the reaction and gives rise to a steeper slope at the first part of the plot leading to a large rate constant. After the lapse of ten to twenty minutes the temperature is lowered to room temperature, and the hydrolysis retarded. The straight line after a break can be assigned to the hydrolysis process at room temperature. Thus, the rate constant for the hydrolysis at room temperature, k_3, is obtained from the slope after the break point. (k_3' denotes the rate constant for the system immediately after dissolution.)

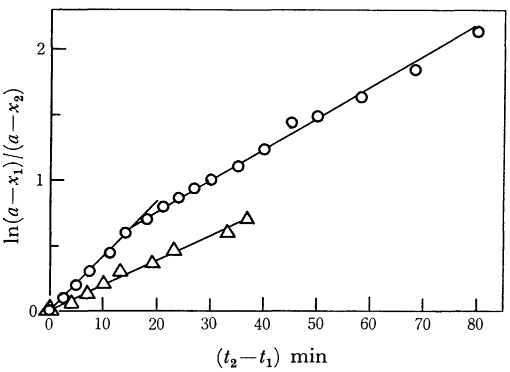


Fig. 8. Plot for the determination of the hydrolysis rate constant of pyrophosphoric acid.
○: 6N HCl solution; △: aqueous solution.

The obtained rate constants are shown in Table 3. The constant depends upon pH and ion concentration of the solution; k_3(6N HCl)$>k_3$(aq. soln.)$>k_3$(3N CaCl$_2$)$>k_3$(6N NaOH). This means that the hydrolysis process is accelerated by the H^+ ion. This is in line with results of several authors.[4-6,8-10] In $CaCl_2$ solution the rate constant is smaller than in aqueous solution. It seems that Ca^{2+} ion as well as pH of this solution affects the hydrolysis rate.[8-10,17]

Sodium Tripolyphosphate. Tripolyphosphate gives a spectrum with three peaks. Peaks M and E decreases their intensity with time, whereas peak O increases. This is shown in Fig. 7. Peak M diminishes in an hour in hydrochloric acid solution. Hydrolysis seems to reach equilibrium two hours after dissolution.

The hydrolysis of tripolyphosphate proceeds in the following pattern.

$$\text{P-O-P-O-P (tripoly-)} \xrightarrow{k_1} \text{P-O-P (pyro-)} + \text{P},$$
$$\xrightarrow{k_3} \text{P}.$$

The rate equations are as follows.

$$dx/dt = -k_1x \text{ or } x_2 = x_1 \exp[-k_1(t_2-t_1)],$$

and $$dy/dt = -k_3y + k_1x \text{ or}$$

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[17] W. Wieker and E. Thilo, *Z. Anorg. Allg. Chem.*, **306**, 48 (1960).

$$y_2 = \frac{k_1 x_1}{k_1 - k_2}\{\exp[-k_3(t_2-t_1)] - \exp[-k_1(t_2-t_1)]\},$$

where x is the concentration of polyphosphate and y pyrophosphate, and their values are given by the peak heights as M and E$-$2M, respectively. The obtained results for the hydrochloric acid solution were $k_1=1.7\times10^{-2}$ min^{-1} and $k_3=0.8\times10^{-2}$ min^{-1}, and $k_1>k_3$. This relation of magnitudes of k's means that the amount of the primary product, pyrophosphate, in the solution increases at first because of slow rate of the second step degradation.

In aqueous solution of sodium tripolyphosphate, hydrolysis is very slow and the rate constant could not be determined although the observation was carried out for 24 hr. Hydrolysis is considerably slowed down in a solution with high pH value.

Polyphosphoric Acid. Both the structure of this compound and the mechanism of hydrolysis are not clear. It is difficult to determine the rate constant for the whole hydrolysis process. However, acceleration of the reaction due to the existence of H$^+$ ion is evident from comparison of the variation of the peak intensity for 6N HCl and aqueous solutions. Peak M disappeared within ten to several tens of minutes.

After the disappearence of peak M, only peak E can be traced. Analysis of the intensity of peak E for 6N HCl solution gives the rate constants $k_3'=5.36\times10^{-2}$ min^{-1} and $k_3=1.04\times10^{-2}$ min^{-1}. For aqueous solution there was no remarkable heat evolution and the rate constant $k_3=9.80\times10^{-3}$ min^{-1} was obtained. The values also show acceleration of the hydrolysis by H$^+$ ion.

Other Phosphates and Phosphoric Acids. Sodium metaphosphate and sodium pyrophosphate undergo hydrolysis in aqueous solution very slowly, but in 6N HCl solution they change to orthophosphoric acid in a day. It is concluded that the H$^+$ ion accelerates hydrolysis for the compounds studies.

The rate constants are summarized in Table 3. They are compared with those obtained by methods other than NMR.[1,7,9,18]

TABLE 3. HYDROLYSIS REACTION RATE CONSTANTS (in min^{-1})

Compound	Solution	Rate constant
Pyrophosphoric acid	6N HCl	$k_3'=4.39\times10^{-2}$
		$k_3=2.50\times10^{-2}$
	aq.	$k_3=1.18\times10^{-2}$
	3N $CaCl_2$	$k_3'=9.80\times10^{-3}$
		$k_3=3.68\times10^{-3}$
	6N NaOH	$k_3'=1.65\times10^{-3}$
		$k_3=1.74\times10^{-4}$
Na-Tripolyphosphate	6N HCl	$k_1=1.7\times10^{-2}$
		$k_3=0.8\times10^{-2}$
Polyphosphoric acid	6N HCl	$k_3'=5.36\times10^{-2}$
		$k_3=1.04\times10^{-2}$
	aq.	$k_3=9.80\times10^{-3}$

k_1 : 1-st order rate constant for Process-1 at room temperature.
k_3 : 1-st order rate constant for Process-3 at room temperature.
k_3': 1-st order rate constant for Process-3 at the temperature of solution immediately after dissolution.

Conclusion

The chemical shifts of phosphorus NMR observed for polyphosphates appear to change with the chain length (so far it is short), the pH as well as the cation of the solution. The spin-spin coupling constant between phosphorus nuclei also depends on the pH of the solution.

The hydrolysis process of various kinds of phosphates was studied by NMR. The NMR gives clear information on the hydrolysis process from the observation of the signal intensities for the phosphorus species in molecules. For simple systems, this information gives the concentration of various molecular species in the course of the hydrolysis.

Analysis of the hydrolysis process with the intensity variation of the NMR signal is relatively simple when the structure of the molecule is known. The obtained values of the rate constant for the hydrolysis can be compared with those obtained by various methods other than NMR and thus the NMR method appears to be very useful.

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