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Synthesis and Characterization of Straight-Chain Oligomers of Methylenediphosphonic Acid

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Received July 8, 1976 AIC60493Q

A mixture of predominantly linear oligomers was produced by condensing an equimolar mixture of methylenediphosphonic acid with its tetrachloride. This mixture was separated by eluting a long cellulose–ether column with a proportional gradient of aqueous triethylammonium bicarbonate. From comparison with the data obtained on a polyphosphate mixture in the same column using the same eluate, as well as from the ^{31}P NMR spectra of the various aqueous fractions, it was found that the linear bis- through the octakis(methylenediphosphonate) anions were separated. The ^{31}P NMR spectra exhibited a natural subdivision into groups of resonances which for these oligomers corresponded to the monomer, the terminal phosphorus atoms of the chains, the next nearest phosphorus atoms, and the remaining middle-position phosphorus atoms. In these spectra the small amounts of simple-ring molecules exhibited sharp single resonances as expected.

Introduction

In a previous study by our group[1] it was shown that methylenediphosphonic acid, $(HO)_2(O)PCH_2P(O)(OH)_2$, may be condensed by dicyclohexylcarbodiimide to give oxygen-bridged linear and cyclic bis(methylenediphosphonic) acids as well as several more condensed cyclic species including the un-ionized birdcage anhydride $P_4O_8(CH_2)_2$ which is the doubly methylene-bridged analogue of phosphorus pentoxide. Unfortunately, methylenediphosphonic acid and its acid salts are found to undergo decomposition upon heating, rather than condensing in a manner similar to that found for the analogous phosphates. Therefore, we decided to look more carefully into an alternative method for condensing methylenediphosphonate anions in order to see whether it would be possible to make straight-chain oligomers. These oligomers should be similar to the even-numbered polyphosphates except for the fact that the alternate bridging oxygen atoms are substituted by methylene groups. In our prior work[1] the condensation was carried out in relatively dilute solution in an organic solvent so that cyclic products would be emphasized. In order to maximize the formation of linear oligomers, the condensation reactions described below were carried out with neat reagents.

Experimental Section[2]

Tetraethyl methylenediphosphonate was prepared by the method of Nylen[3] and methylenediphosphonic acid was made from it by hydrolysis. Methylenediphosphonyl tetrachloride was synthesized according to Richard et al.[4] Triethylamine from Fisher Scientific Co. was freshly distilled over sodium, with the fraction coming off between 80 and 90 °C being collected. All other reagents were CP grade.

Attempts to condense methylenediphosphonic acid thermally by driving off water proved unsuccessful since the products had a strong phosphine odor and, in fresh aqueous solutions, exhibited ^{31}P NMR patterns showing resonances at −20.1, −30.1 and −57.3 ppm, values lying downfield from the chemical shift of the monomer. However, polymerization was successfully carried out by heating together equimolar amounts of methylenediphosphonic acid and its tetrachloride at 130 °C. When the temperature rose above 110 °C, the mixture started to froth with evolution of gaseous hydrochloric acid (which was shown to be present by its acidity and a silver test for the chloride content). The resulting ^{31}P NMR spectrum of a fresh aqueous solution exhibited resonances in the expected range[1] of −16 to −6 ppm. In repeating this preparation, it was found convenient to add triethylamine to pick up the HCl produced. When the amine was added to the mixture of the reagents, it was found that some polymerization would occur without heating. However, the NMR patterns of fresh aqueous solutions of the product mixtures were not appreciably changed whether the amine was added before or after heating but prior to the dissolution in water. Note that, if the condensation had led to branching in the resulting molecular structures, the branches would be expected to undergo rapid hydrolysis in aqueous solution and hence would not be observed. Likewise any chloro groups remaining after condensation would also be hydrolyzed rapidly into oxyacid functions.

The nuclear magnetic resonance (NMR) data were taken on aqueous solutions with a Varian XL-100-15 spectrograph using broad-band decoupling of the methylene protons. The ^{31}P NMR chemical shifts were referenced to 85% orthophosphoric acid, with downfield shifts being designated as negative. The simulation of the observed spectra was achieved with the computer programs NMRIT and NMRENI by Swalen.[5]

General methods previously described by us for separating the condensed phosphates[6] by column chromatography were employed for the oligomers of methylenediphosphonic acid. In this case, a column 193 cm × 2.5 cm was eluted using an 18-L linear-gradient (0.2–1.0 M) triethylammonium bicarbonate solution to give 700 15-mL cuts, every tenth one of which was analyzed for total phosphorus.[7] The analytical results showed that eight separable fractions (corresponding in one run to cuts 50–114, 118–178, 198–266, 278–337, 368–398, 420–458, 475–537, and 575–648) were obtained. The last fraction may have consisted of a collection of the larger molecular anions which are not individually separable by this column. However, as opposed to a vitreous sodium polyphosphate which exhibited extensive tailing in the last fraction obtained, the condensed methylenediphosphonate mixture showed little tailing in the last fraction.

After the individual cuts were combined into the eight fractions, the volume of each fraction was reduced to ca. 5 mL from its original size of 450–1100 mL in a rotary vacuum evaporator at 24 °C and a pH of ca. 8. Then 10-mL portions of methanol were added and evaporated to dryness in five consecutive treatments designed to remove the triethylammonium bicarbonate by volatilization. Finally the residue was dissolved in 1 mL of water and the pH was immediately adjusted to 10.8 with concentrated NaOH. The resulting solutions were found to be stable for months at room temperature.

Results and Discussion

A preliminary study was carried out on the hydrolysis of the oligomeric mixtures in aqueous solution as a function of pH before attempting to separate the oligomeric mixture of the condensed methylenediphosphonic acids. This work showed that the reaction was acid catalyzed but not base catalyzed so that it seemed clear that, whenever possible, the solutions should be kept alkaline. A plot of the molarity of the eluate vs. the order of appearance of the eight fractions recovered when the condensed methylenediphosphonic acid mixture was put through the ion-exchange column is compared in Figure 1 with similar results obtained for a polyphosphate mixture in the same column under the same conditions. The assignment of the number of phosphorus atoms in the linear oligomeric methylenediphosphonate anions is made in Figure 1 on the basis of (a) the close correspondence between these compounds and their phosphate analogues and (b) the fact that increasingly large molecules should be eluted at later times. Obviously the molecule having two phosphorus atoms in the chains is the starting compound, the uncondensed methylenediphosphonate, a fact that was readily demonstrated experimentally. The molecular structure of the anion of the pentakis oligomer is shown here as an example

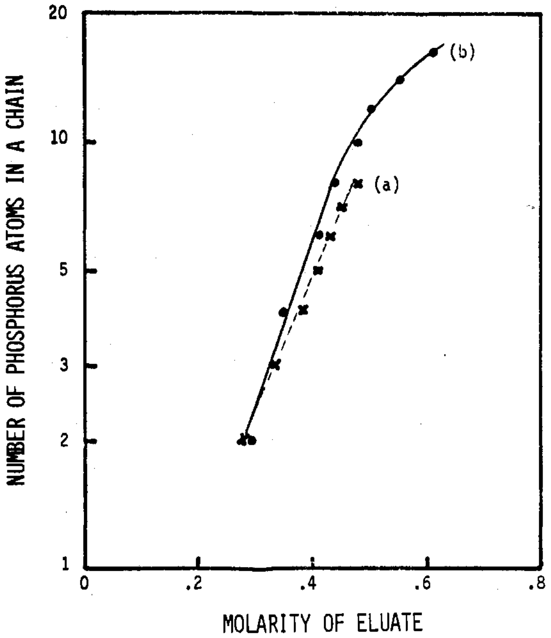
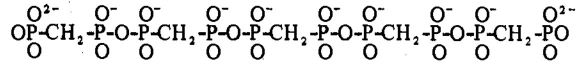


Figure 1. Logarithm of the number of phosphorus atoms in (a) polyphosphate and (b) poly(methylenediphosphonate) chains vs. the molarity at which the individual chain compounds were eluted. The final fraction in (b) probably consisted of a mixture of oligomers having 16 or more phosphorus atoms per molecule.



$$\mathrm{O}\overset{\mathrm{O}^{2-}}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{CH}_2\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{O}\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{CH}_2\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{O}\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{CH}_2\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{O}\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{CH}_2\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{O}\text{-}\overset{\mathrm{O}^-}{\underset{\mathrm{O}}{\mathrm{P}}}\text{-}\mathrm{CH}_2\text{-}\overset{\mathrm{O}^{2-}}{\underset{\mathrm{O}}{\mathrm{P}}}\mathrm{O}$$

NMR spectra of the individual fractions corresponding to the bis- through the octakis(methylenediphosphonate) anions at pH 10.8 are shown in Figure 2. Of course, the uncondensed methylenediphosphonic acid shows just a single proton-decoupled ^{31}P NMR resonance peak which appears at −16.7 ppm at this pH. The symmetrical pattern of the proton-decoupled ^{31}P NMR spectrum of the bis(dimethylenephosphonate) anion is consistent with the structure of this highly symmetrical chain based on four phosphorus atoms. As expected, this spectrum is quite similar to that[6] of the corresponding linear tetraphosphate anion. The NMR spectra of the fractions that came out later from the ion-exchange column are all higher order spectra that are reasonably similar to those[6] of the corresponding chain polyphosphates. Thus, the middle-group region of these spectra, corresponding to the region centered around −9 ppm, exhibits an increasing proportion of the total peak areas as the chain length of the methylenediphosphonate oligomers increases. The major difference between the ^{31}P

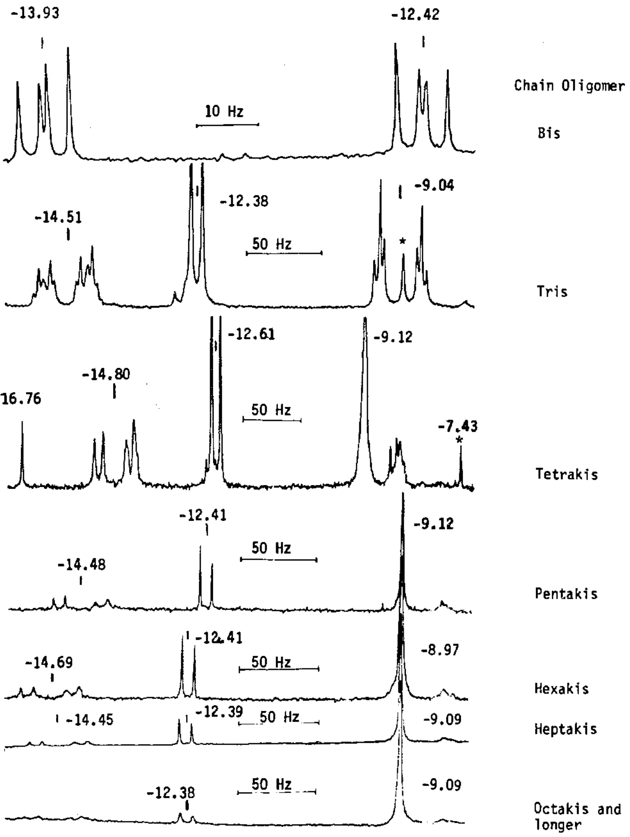


Figure 2. ^{31}P proton-decoupled NMR spectra of the second through the eighth fraction. The midpoint chemical shift values are in ppm. The resonances denoted by an asterisk correspond to cyclic anions, presumably of the same size of the chain oligomer noted.

spectra of the polyphosphates and those of the methylenediphosphonate oligomers containing the same number of phosphorus atoms per anion lies in the fact that in addition to the spectral region for the terminal phosphorus atoms, there is also a spectral region corresponding to the phosphorus atoms which are next nearest neighbors to the terminal phosphorus atoms (i.e., are in the penultimate positions). Since, in the oligomeric methylenediphosphonate anions, the numbers of end and penultimate phosphorus atoms are identical, peak areas do not afford a clue to making this assignment which must be derived from analysis of the NMR fine structure. To a first-order approximation, one would expect that the resonance corresponding to the terminal phosphorus atom in the tris and longer chains would look like a 1:1 doublet since it is primarily coupled only to its single nearest-neighbor phosphorus. On the other hand the penultimate pattern would be expected to be a doublet of multiplets since it is coupled (a) through a methylene group to the terminal phosphorus atom and (b) through a bridging oxygen to the third phosphorus from the end of the chain. On this basis, the resonance region centered around −12.5 ppm at pH 10.8 should correspond to the terminal phosphorus, while that around −14.5 ppm would be attributed to the penultimate. These assignments were tested for the bis- and tris(methylenediphosphonate) chain anions by computer fitting[5] of the coupling constants and chemical shifts, and the resulting values are shown in Table I.

In the preliminary ^{31}P NMR studies of the oligomeric mixtures it was observed that the NMR patterns exhibited considerable change with pH, much more change than is found for the polyphosphates. Therefore the pH variation of the NMR pattern of the tris(methylenediphosphonate) anion was investigated as a function of pH and the results are depicted in Figure 3. It should be noted in this figure that the position of the middle-group resonances changes very little with pH, moving only about 0.25 ppm upfield when going from pH 7.0 to pH 10.8. This is to be expected, of course, since the weakly acidic hydrogens lie at the ends of the chains so that the major influence of pH changes on the middle-group phosphorus atoms can be considered to be essentially a solvent effect. Upon going from pH 7.0 to pH 10.8, there is a pronounced upfield shift of around 95 Hz for the end-phosphorus atoms, whereas in the same pH range, the chemical shift of the penultimate phosphorus is even larger and in the opposite direction, corresponding to a downfield change of 153 Hz. These findings are summarized in Figure 4.

Table I. Fitted ^{31}P NMR Parameters for the Bis- and Tris(methylenediphosphonate) Anions

Parameter	Bis pH 10.8	Tris pH 10.8	Tris pH 7.0
Chem shift, ppm			
End, δ_1	−12.42	−12.38	−14.70
Next to end, δ_2	−13.93	−14.51	−10.72
Middle, δ_3 for tris		−9.04	−9.31
Coupling const, Hz			
J_{12}	7.4	7.7	8.6
J_{13}	0.9	0	0
J_{23}	14.2	28.0	28.1
J_{24}	0.9	0	0
J_{34}	7.4	7.2	6.4
J_{45}		28.0	28.1
J_{56}		7.7	8.6

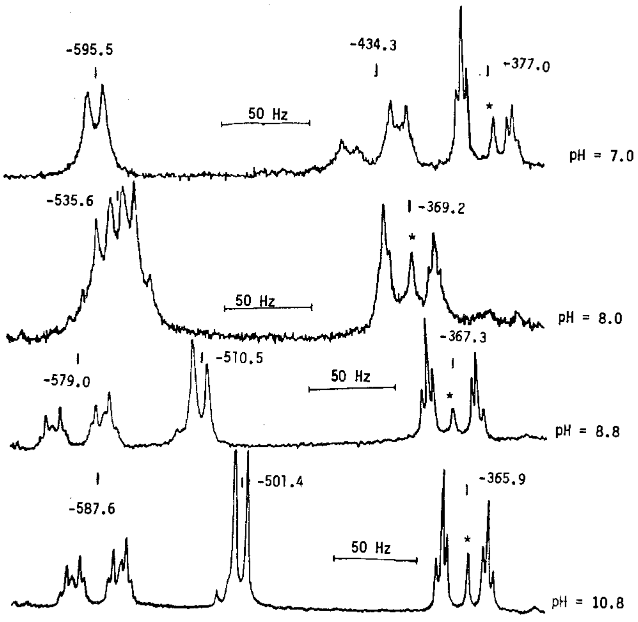


Figure 3. Effect of pH on the ^{31}P proton-decoupled NMR spectra of the tris(methylenediphosphonate) anion. The midpoint chemical shift values of each region are reported in Hz. The peak denoted by an asterisk corresponds to the cyclic tris anion, the chemical shift of which (at −367 Hz) is little affected by the pH changes.

Even though time averaging was achieved by the Fourier-transform technique (with cycling times of ca. 3 s) and proton decoupling was employed, it turned out that the NMR area ratios corresponding to the end-, the penultimate-, and the middle-phosphorus atoms agreed quite well with the values to be expected from a linear-chain structure (e.g., for the hexakis oligomer this ratio was found to be 1.0:1.0:3.9 as compared to the theoretical value of 1:1:4). We believe that this good correspondence is due to several factors. First, each phosphorus atom in these various oligomeric structures has a single nearest-neighbor methylene group, and, second, at pH 10.8 each phosphorus is exposed to about the same protonic

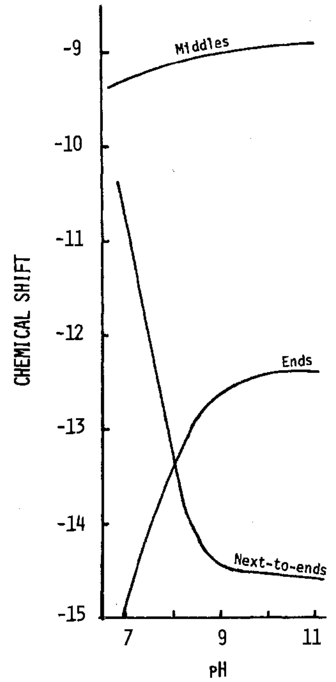


Figure 4. Variation of the ^{31}P chemical shifts of the end, next-to-end, and middle groups of the tris(methylenediphosphonate) anion as a function of pH in aqueous solution.

environment due to the solvent as are the other phosphorus atoms in the structure. In other words, it would seem that the nuclear Overhauser enhancement under these experimental conditions may well be about the same for all of the phosphorus atoms in the molecule. Similarly, it would appear that the response of each of the phosphorus nuclei to the various experimental parameters associated with the radiofrequency pulsing is about the same with respect to the peak areas. Careful time-averaged area-measurement studies on the ^{31}P spectra of the tris- and heptakis(methylenediphosphonate) anions at pH 10.8 without proton decoupling and with prolonged delay times (10 s) between pulses were found to give equivalent results, i.e., peak areas close to 1:1:1 and 1:1:4, respectively.

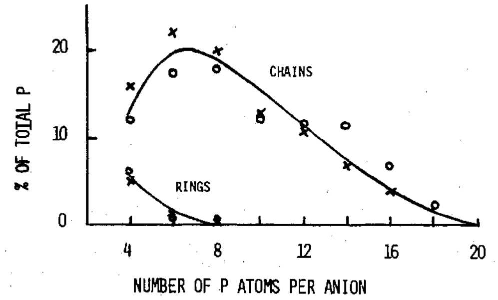


Figure 5. Observed product distribution from the condensation of tetraethyl methylenediphosphonate with methylenediphosphonyl tetrachloride. The circles and crosses represent different runs; and the last two points of each run were arbitrarily distributed to represent the final fraction.

The ^{31}P NMR spectrum of the ion-exchange fraction containing the linear bis(methylenediphosphonate) anion also exhibited a single relatively sharp resonance peak at −6.80 ppm, and we have assigned this resonance to the cyclic bis(methylenediphosphonate) anion. Prior studies on aqueous solutions of the chain and ring polyphosphates[6,8] using the same kind of ion-exchange column and eluate employed here have shown that ring and chain molecule anions having the same number of phosphorus atoms per structure will appear in the same broad fraction. In the center of the middle-group region of the spectrum of the linear tris(methylenediphosphonate) anion there was a single rather sharp resonance (see Figure 2) at −9.01 ppm which could not be fitted in the mathematical analysis of the higher order spectrum of this chain oligomer. Attempts to force the computer program to accept this peak as part of the spectrum always resulted in splitting up of this assignment into two segments which moved apart upon reiteration so as to coalesce into the middle-group resonances on either side of it. Therefore, we also attribute this resonance to a cyclic structure, the *cyclo*-tris(methylenediphosphonate) anion. Another relatively sharp middle-group resonance lying at −7.43 ppm was also observed in the fraction containing the linear tetrakis(methylenediphosphonate) anion, and we ascribe this peak to the cyclic tetrakis analogue. Thus, under the experimental conditions, it would appear that the chemical shifts of the cyclic methylenediphosphonate molecule anions lie in the order tris, tetrakis, and bis, going to higher fields. Such nonlinear variations of chemical shift with ring size has previously been observed and commented upon for the cyclic metaphosphates.[8]

The ^{31}P NMR data show that the condensation between tetraethyl methylenediphosphonate and its tetrachloride in the absence of a solvent led to about 20% of the total phosphorus appearing as the unreacted monomer, with the remainder in linear and cyclic oligomers. Of these, only the linear and cyclic bis structures have been previously described.[1] The observed product distribution is shown in Figure 5, from which it can be seen that the most prevalent chain molecule in the reaction product mixture is the tris oligomer, which corresponded to ca. 20% of the total phosphorus, whereas the most prominent ring molecule is the cyclic bis structure, which corresponded to ca. 5% of the total phosphorus.

Acknowledgment. We thank the National Science Foundation for partial funding of this work under Grants MPS 71-02886 A04 and CHE76-04287. We also appreciate the financial support of Mr. Nweke as a graduate teaching assistant at Vanderbilt University.

Registry No. Bis(methylenediphosphonate), 61570-58-9; tris(methylenediphosphonate), 61570-59-0; tetrakis(methylenediphosphonate), 61570-60-3; pentakis(methylenediphosphonate), 61570-61-4; hexakis(methylenediphosphonate), 61570-62-5; heptakis(methylenediphosphonate), 61570-63-6; octakis(methylenediphosphonate), 61570-64-7; ^{31}P, 7723-14-0.

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