25% excess) dispersed in about 200 ml of triglyme. While the reaction mixture was refluxed, the product vapors were taken off under vacuum and allowed to pass through cold traps at −23, −78, and −196°. The $P(CH_3)_3CH_2$ (2.64 g) was obtained from the −78° trap. The mass spectrum had a parent peak at m/e 90. The proton NMR spectrum of the neat product showed two doublets, one at δ −0.7 with respect to TMS, J = 6 Hz (intensity 1), and the other at δ 1.38 with respect to TMS, J = 12 Hz (intensity 4.5). Trimethylphosphineimide was isolated in an attempt to prepare $P(CH_3)_3CH_2$ in liquid ammonia. Tetramethylphosphonium iodide (15.4 g) was added to 100 mmol of freshly precipitated KNH_2 in about 100 ml of liquid ammonia. The reaction mixture was stirred for 1 hr when the ammonia had evaporated. The volatile products were passed through cold traps at −23, −78, and −196°. An oily material which partially solidified upon standing and which evolved CH_4 was collected in the −23 and −78° traps. After 2 days, 0.28 g of $P(CH_3)_3NH$ was sublimed from the traps, leaving a viscous, nonvolatile oily residue. The melting point (58–59°) agreed with the literature[15] and the mass spectrum showed a parent peak at m/e 91 and a strong, pressure-dependent P + 1 peak. A proton NMR spectrum of the neat material showed a singlet at δ 0.1 relative to TMS of intensity of 1 and a doublet at δ 1.65 relative to TMS with J = 13 Hz and an intensity of 9. Trimethylphosphine oxide was prepared from $POCl_3$ and CH_3MgBr;[16] its melting point (136–138°) agreed with the literature value (137.5–138.5°).

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Registry No. $P(CH_3)_3 \cdot BH_3$, 1898-77-7; $P(CH_3)_3CH_2$, 14580-91-7; $P(CH_3)_3NH$, 15107-02-5; $P(CH_3)_3O$, 676-96-0; $TiCl_4$, 7550-45-0; $VOCl_3$, 7727-18-6; CrO_2Cl_2, 7791-14-2; MnO_3Cl, 15605-27-3; $SiCl_4$, 10026-04-7; $POCl_3$, 10025-87-3; SO_2Cl_2, 7791-25-5; $Si(CH_3)_4$, 75-76-3; $S(CH_3)_2O_2$, 67-71-0; SiF_4, 7783-61-1; POF_3, 13478-20-1; SO_2F_2, 2699-79-8; ClO_3F, 7616-94-6; SNF_3, 15930-75-3; KNH_2, 17242-52-3; tetramethylphosphonium iodide, 993-11-3.

References and Notes

(1) U. Gelius, *Phys. Scr.*, **9**, 133 (1974).

(2) The following references provide evidence that the relaxation energy associated with the core ionization of an atom is closely related to the number and types of atoms bonded to the atom: D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972); W. L. Jolly and W. B. Perry, *J. Am. Chem. Soc.*, **95**, 5442 (1973).

(3) This assumption is obviously justified for the methyl and chlorine compounds, in which an increase in the nuclear charge of the central atom is accompanied by an increase in the electronegativity of one of the ligand atoms. The justification is not obvious in the case of the fluorine compounds unless one assumes that transfer of a proton from the nucleus of one atom to that of a second atom is accompanied by the transfer of less than a full electron to the second atom. However, various charge calculation methods (CNDO, extended Hückel, and electronegativity based) show that the assumption is valid for all the compounds in Table II.

(4) The formal charge is the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms.

(5) W. L. Jolly and W. B. Perry, *Inorg. Chem.*, **13**, 2686 (1974).

(6) W. B. Perry and W. L. Jolly, *Inorg. Chem.*, **13**, 1211 (1974).

(7) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, pp 453–456.

(8) H. H. Sisler, *Inorg. Synth.*, **2**, 205 (1946).

(9) T. S. Briggs, *J. Inorg. Nucl. Chem.*, **30**, 2866 (1968).

(10) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed, Academic Press, New York, N.Y., 1963, p 166.

(11) Reference 10, p 1265.

(12) Reference 10, p 385.

(13) R. Thomas and K. Eriks, *Inorg. Synth.*, **9**, 59 (1967).

(14) R. Koester, D. Simie, and M. A. Grassberger, *Justus Liebigs Ann. Chem.*, **739**, 211 (1970).

(15) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

(16) A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).

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Full Anhydrization of Methylenediphosphonic Acid and of Phosphoric Acids by a Carbodiimide

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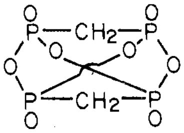
Methylenediphosphonic acid may be condensed by dicyclohexylcarbodiimide through a number of intermediate species to a compound identified by ^{31}P NMR as the unionized birdcage anhydride



which is a phosphonic analog of phosphorus pentoxide. The intermediate molecular species have been identified and the course of the reaction has been studied and discussed. As part of this work, we also have been able to condense various phosphoric acids to what appears to be a carbodiimide adduct of the birdcage P_4O_{10} molecule.

Introduction

A considerable body of evidence[1–6] has been developed to show that, under the usual laboratory conditions, esterifications of phosphoric acids and their esters (both simple and biological) mediated by carbodiimides and related condensing agents do not occur in the presence of an amine base whereas P–O–P condensation of these acids and esters proceeds readily under these conditions. However, in a study[7] from our group, it was shown that, in spite of this well-accepted conclusion, methylenediphosphonic acid—a close analog of pyrophosphoric acid—was easily esterified by isopropylidineadenosine to make the methylene-bridged analog of adenosine diphosphate, ADP, in high yield. Because of this finding, it seemed desirable to investigate the fundamental inorganic chemistry of the carbodiimide-induced condensation of the simple methylenediphosphonic acid $[(HO)_2(O)P]_2CH_2$. In this work, described herein, we found that the condensation could be driven to completion, with all possible anhydride linkages being made. This emboldened us to attempt the synthesis of the P_4O_{10} molecule by a chemical condensation in solution of a simple phosphoric acid. Up to now, there has been no evidence for condensation of any phosphoric acid all the way to phosphoric anhydride and the dissolution of phosphorus pentoxide in a solvent has always (or almost always[8]) led to scission of P–O–P linkages.

Experimental Section

Crystalline methylenediphosphonic acid was prepared according to the literature[7,9] and all other reagents were purchased commercially.

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The tetramethylurea was purified according to the method we have previously described,[10] and the ^{31}P nuclear magnetic resonance (NMR) measurements[11-13] and their mathematical interpretations[14,15] were carried out in the same manner as employed in previous studies.[15] The ^{31}P NMR data were generally taken with broad-band decoupling of the methylene protons since the NMR spectra obtained without decoupling are usually uninterpretable either because of extreme complexity or loss of resolution due to the overlap of signals. However, we did find that J_{PCH} exhibits a value around 18 Hz for all of these molecules.[16] Because of the extreme hygroscopicity of the composition study, it was necessary at all times to avoid[15] contamination by trace amounts of moisture. Because of inadvertent introduction of water from sealing the glass tubes with a torch, we did not melt the glass together but instead used tight polyethylene covers for the NMR tubes employed in this work.

Isolation of New Compounds. Variants of our previously published[17] separations technique were employed. In these procedures, the reaction was quenched by dilution with anhydrous acetone and then anhydrous sodium iodide in acetone was added in order to precipitate the sodium salts of methylenediphosphonic acid and its condensation products. Although several variations of this technique were employed, it was always found by ^{31}P NMR that dissolution of the precipitated material in an aqueous medium led only to the simple methylenediphosphonate anion, I, plus the chain, II, and/or ring, III, anions resulting from condensing two molecules of I. By use of an anion-exchange column,[17] the sodium salt of II, $Na_6P_4(CH_2)_2O_{11}$, and of III, $Na_4P_4(CH_2)_2O_{10}$, were isolated. These salts exhibited the proper ^{31}P NMR patterns (Table I) when dissolved in water.

Results and Discussion

Basic Condensation of Methylenediphosphonic Acid. Preliminary experiments showed that several different carbodiimides would lead to condensation of methylenediphosphonic acid in the presence of any of several tertiary aliphatic amine bases present in amounts ranging from zero to several moles per phosphorus equivalent. However, most of the work reported herein has been carried out on a composition consisting of 200 mg (2.1 mmol) of methylenediphosphonic acid dissolved in a mixture of 20 ml of tetramethylurea with 0.48 mg (2.0 mmol) of tri-*n*-butylamine to which 2 g (10 mmol) of barely molten dicyclohexylcarbodiimide was added. With continued stirring, the solution remains clear for several minutes at room temperature, exhibiting barely detectable warming. Then the urea which results from hydration of the carbodiimide precipitates as large, well-defined crystals. The course of the overall reaction was followed by ^{31}P NMR and the resulting kinetic curves showing the distribution of the total dissolved phosphorus among the various species are presented in Figure 1. Note that analysis of the precipitates showed no phosphorus compound to be precipitated at any time during the course of the reactions.

The curve labeled I corresponds to the single ^{31}P NMR peak, appearing at −14.8 ppm im this particular solvent, due to the methylenediphosphonate anion. The curve labeled II corresponds to a multiplet in the end-group region of the phosphonate ^{31}P NMR spectrum plus an equivalent multiplet in the middle-group region. From the similarity of this NMR pattern to that of the tetraphosphate anion,[16] it was clearly apparent that structure II is the linear-chain product obtained from condensation of two molecules of methylenediphosphonic acid. The NMR pattern of this product and of the other molecules observed in this study was analyzed in detail[18,19] and simulated by a computer[14,15] to give the ^{31}P NMR parameters reported in Table I. The structures of all of these compounds are presented in Figure 2.

The curve in Figure 1 corresponding to the minor constituent III corresponds to a single resonance line which has been assigned to the cyclized dimer of methylenediphosphonic acid. A symmetric adduct of this cyclic dimer with two molecules of the carbodiimide is the structure which has been assigned to compound V, again on the basis of a full analysis of its aa'bb' NMR pattern. In the structure given for this compound in Figure 2, each of the two substituted phosphorus atoms is shown as being directly bonded to a carbodiimide nitrogen atom. This structural feature is deduced by analogy to the trimetaphosphate–carbodiimide adducts, the structures of which have been carefully established from their ^1H and undecoupled ^{31}P spectra.[15] Moreover, irradiation of the methine region of the ^1H spectra of compounds IV and V did lead to partial decoupling of the ^{31}P multiplets; however, the resulting spectra are still too complicated and poorly resolved to be rigorously interpreted, due to phosphorus coupling with the methylene protons of the bridging CH_2 groups. The methine protons involved in the methine coupling presumably reside on the N-substituted carbon atoms of the cyclohexane rings so that the spin system is PNCH (J = 9–12 Hz). Thus, although the ^1H and undecoupled ^{31}P spectra were inaccessibly complicated for compound V (and also IV), the substitution of the phosphoryl oxygen by the carbodiimide nitrogen in this kind of structure is assumed to be analogous to that known to occur in the condensation of pyrophosphoric acid.

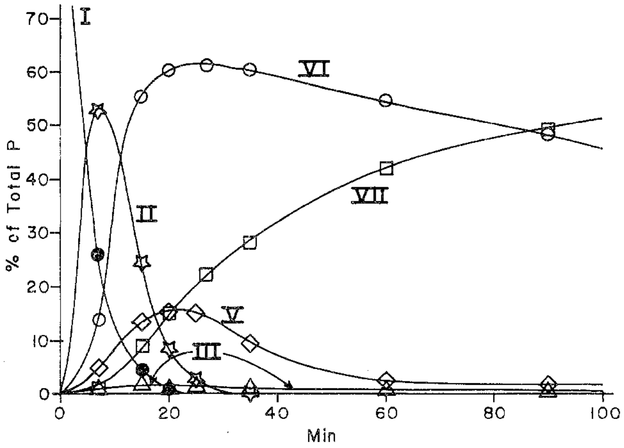


Figure 1. Time course for the condensation of methylenediphosphonic acid by dicyclohexylcarbodiimide in the presence of tri-*n*-butylamine. The structures of the compounds corresponding to each numeral are presented in Figure 2. At 20 min into the reaction, resonances corresponding to IV can just be detected. This is the point in the time course just after II has maximized but before either V or VI has maximized. The latter two appear to maximize at about the same time, perhaps with V coming slightly before VI. As near as can be determined, the entire sequence given in this figure also holds for condensation in acidic media, except that in acid the reaction is much accelerated.

The ^{31}P NMR pattern corresponding to compound VI exhibited an appearance similar to that of the condensed phosphate in which two tetrametaphosphate rings are joined by a bridging oxygen atom.[15] This indicates that compound VI consists of two cyclic dimers connected by a single oxygen bridge. Similarly the NMR pattern of compound VII implies that the structure of this molecule corresponds to a cyclic dimer internally bridged by an oxygen atom. The NMR parameters resulting from the detailed analysis of the respective NMR patterns are in accord with these assignments and are presented in Table I while the structures are given in Figure 2.

The set of reactions shown in Figure 1 continues for several hundred minutes, with compounds V and VI disappearing in favor of VII, which finally represents essentially all of the total phosphorus originally employed in this reaction. A diagram of the reactions is presented in Figure 2 in which the condensing action whereby the carbodiimide is converted into its urea is symbolized by $-H_2O$ while addition or subtraction of the carbodiimide to the condensed diphosphonate molecules is represented by +DCC or −DCC and subtraction of its urea by −DCU. Although compound IV does not appear among the kinetic curves shown in Figure 1, a barely detectable NMR pattern was observed after the reactions had proceeded for

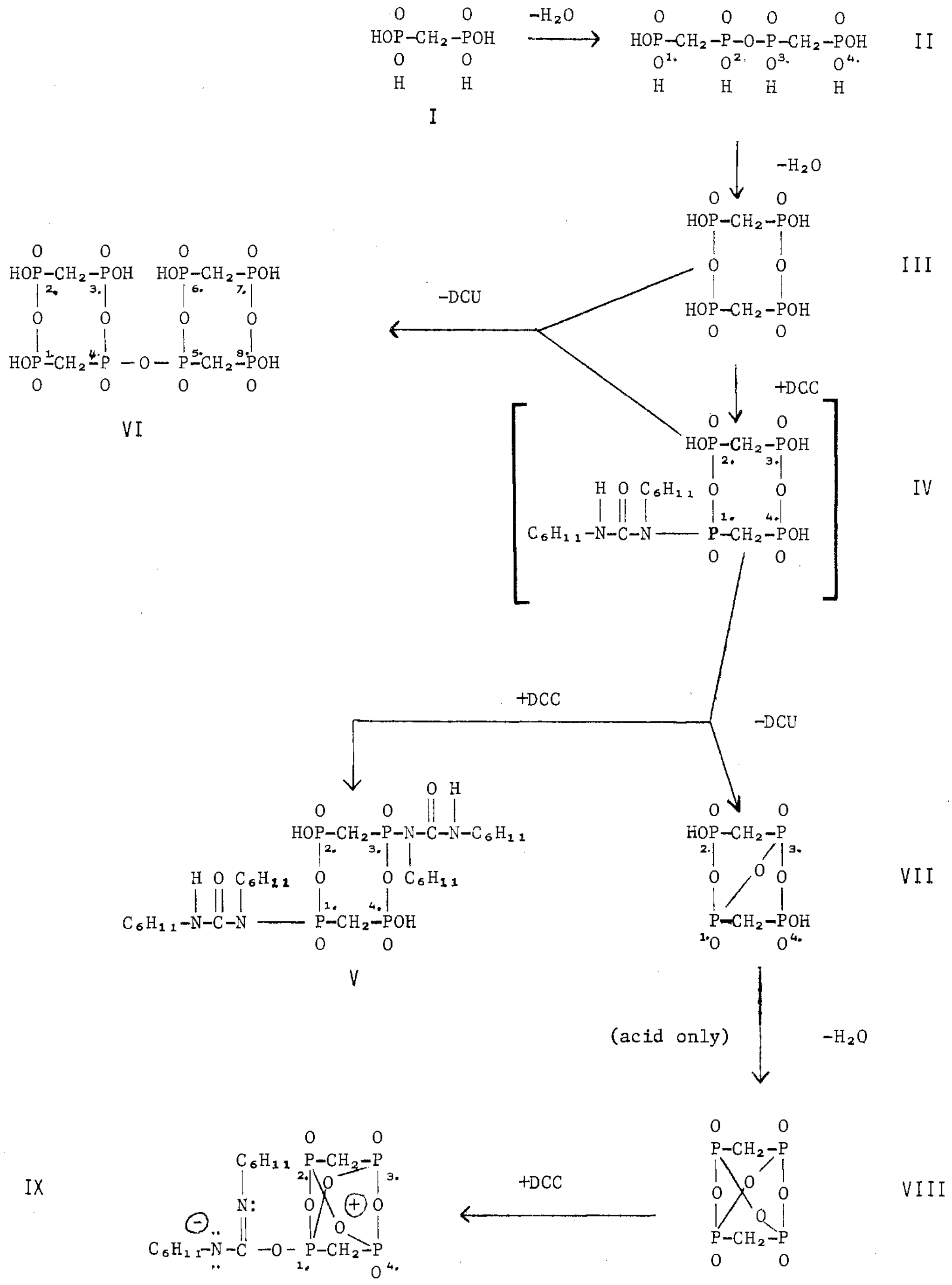


Figure 2. Reaction sequence and molecular species present in the dicyclohexylcarbodiimide-mediated condensation of methylenediphosphonic acid. The phosphorus atoms of each molecular type depicted are numbered to correspond to the ^{31}P NMR parameters given in Table I, and the phosphonates are shown in their protonic forms. DCC stands for dicyclohexylcarbodiimide, $C_6H_{11}NCNC_6H_{11}$; DCV stands for its urea, $C_6H_{11}NHC(O)NHC_6H_{11}$; and $-H_2O$ represents the equation DCC + H_2O (of composition) → DCU.

about 20 min and this was found to correspond rather well to the skewed quartet which was estimated for this structure by extrapolation of all of the available data obtained for the other condensed phosphonate structures. The extrapolated NMR parameters are presented in Table I. This pattern was also observed fleetingly in some of the preliminary studies.

According to the reaction scheme of Figure 2, the condensation leading from I to II must surely involve a carbodiimide adduct; but this adduct was never present in sufficient concentration to be detected. A similar situation is found for the condensation whereby II is converted into III, and these findings are in accord with the results obtained with the phosphate analogs where adduct intermediates were not observed until a degree of condensation corresponding at least to the metaphosphate composition was achieved.[15] There are undoubtedly scrambling reactions (occurring along with the condensation) which are not shown in Figure 2. We suggest this because in the condensed phosphates the rate of the scrambling process at the metaphosphate composition or at even higher degrees of condensation are extremely high in this solvent system, often being faster than the condensation process itself.[13] Thus, it seems reasonable for compound VI to reorganize to give III plus VII. Also, a reorganization process must be operating between compounds V, VI, and VII since both V and VI are converted to VII at about the same rate—a rate which accelerates with increasing degree of condensation.

Explanation of Esterification Results. In prior work, we have found that phosphate condensation in the presence of an amine

Table I. ^{31}P Chemical Shifts and Coupling Constants Determined for the Phosphatic Components of the Carbodiimide-Mediated Condensation of Methylenediphosphonic Acid

Phosphonate[a]	^{31}P chem shifts,[b] ppm			Coupling constants,[c] Hz
	Chain terminal	Interior chain	Cross-linking points	
I	−14.8 (−16.8)			
II	$P_1 = P_4$, −13.2 (−15.4)	$P_2 = P_3$, −4.9 (−7.4)		$J_{1,2} = J_{3,4} = 12.6$ $J_{2,3} = 19.3$
III		−5.9[d]		
IV		P_1, −7.0[d] $P_2 \approx P_4$, −6.1[d] P_3, −5.0		$J_{1,2} = 29.4$ $J_{1,4} = 6.2$ $J_{2,3} = 6.0$ $J_{3,4} = 28.0$
V		$P_1 = P_3$, −7.0 (−3.8) $P_2 = P_4$, −6.1 (−2.9)		$J_{1,2} = J_{3,4} = 29.8$ $J_{1,4} = J_{2,3} = 6.2$
VI		$P_1 = P_8 \approx P_3 = P_6$, −3.27 (−4.26) $P_2 = P_7$, −4.57 (−5.56)	$P_4 = P_5$, 4.20 (8.00)	$J_{1,4} = J_{5,8} = 4.2$ $J_{1,2} = J_{7,8} = 29.7$ $J_{2,3} = J_{6,7} = 6.0$ $J_{3,4} = J_{5,6} = 31.3$ $J_{4,5} = 29.8$
VII		$P_2 = P_4$, −2.22	$P_1 = P_3$, 2.40 (6.31)	$J_{1,2} = J_{1,3} = J_{3,4} = 28.5$ $J_{1,4} = J_{2,3} = 12.3$
VIII			(6.03)	
IX			P_1, (5.48) $P_2 = P_3$, (6.03) P_4, (6.02)	$J_{1,2} = J_{1,3} = 19.0$ $J_{2,4} = J_{3,4} = 19.0$ $J_{1,4} = J_{2,3} = 7.1$

[a] Refer to Figure 2 for the numbering of the P atoms for each molecule. [b] The ^{31}P resonance frequency is 36.43 MHz; the reference was 85% orthophosphoric acid, and positive chemical shifts were associated with increasing field strengths as is customary in ^{31}P NMR spectroscopy.[16] The numbers in parentheses refer to the shifts in acidic solvents. In these pseudo-first-order spectra the appearance of the multiplets is quite sensitive to the precise values of the chemical shifts so that it is often necessary to calculate a given molecular spectrum several times in interpreting spectra. Because of this chemical shift dependent variability in the appearance of the ^{31}P phosphonate multiplets the individual experimental spectra have not been presented. [c] As well as can be determined, the coupling constants do not change appreciably with protonation of the phosphonates as the chemical shifts may; therefore, only the coupling constants determined in the basic solvent are reported. Coupling to the methylene protons of the bridging CH_2 groups, J_{PCH}, is about 18 Hz in all cases and that to the methine protons of the cyclohexane ring, J_{PNCH}, is 9–12 Hz. [d] Not detectable in the acid solvent.

leads to the trimetaphosphate anion which, upon further reaction, makes N-substituted phosphorylureas instead of producing cyclic structures containing branch groups.[15] On the other hand, acid condensation of the phosphates gives the tetrametaphosphate anion which readily undergoes further condensation to give ultraphosphate molecules,[18] most of which contain more than one branch group in a relatively small molecular structure. It is these branch groups that have the capacity of undergoing facile esterification. Because of the well-known unreactivity of the C–P bond, the presence of the $-CH_2-$ bridge in methylenediphosphonic acid necessarily precludes the formation of a cyclic molecule having three phosphorus atoms per ring, whereas, the ring containing four phosphorus atoms is essentially the sole product corresponding to the metaphosphate degree of condensation. This four-phosphorus intermediate readily converts to branched-cyclic structures which are the phosphonic acid analogs of avidly esterifiable ultraphosphates. This explains the "anomalous" esterification involved in making[7] the methylene-bridged analog of adenosine diphosphate (see the Introduction).

Acidic Condensation of Methylenediphosphonic Acid. If the condensation is carried out without the addition of any amine so that the solution is acidic, the reaction proceeds very rapidly to give a single sharp ^{31}P NMR resonance in the phosphonate branch-group spectral region at +6 ppm in this medium. This signal, however, is transient and is converted over the course of several minutes into an envelope, centered at the same position, which exhibits four barely resolved shoulders. The sharp peak, VIII, is consistent with a completely condensed dimer of methylenediphosphonic acid—a structure which may be derived formally by substituting two opposing oxygen bridges in the P_4O_{10} molecule by methylene bridges. As would be expected for such a fully condensed structure, its NMR chemical shift is the farthest upfield of any chemical shift in this family of phosphonates, being about 2 ppm upfield of the branch group in VI. We attribute the time-dependent broadening of this signal to the formation of a 1:1 carbodiimide adduct, for which the simulated spectrum gives the NMR parameters shown for compound IX in Table I. It is important to note that a 2:1 or a 4:1 adduct cannot be mathematically accommodated to the observed envelope, using any reasonable set of NMR parameters.

In attempting to slow down the acid condensation of methylenediphosphonic acid, we employed less than stoichiometric amounts of the dicyclohexylcarbodiimide. Under these conditions a precipitate is instantly formed upon addition of the carbodiimide—a precipitate which by analysis is seen to be a 1:1 adduct or other 1:1 reaction product (perhaps even a simple salt) formed between these two reagents. However, extensive signal averaging of the ^{31}P NMR spectrum corresponding to the phosphonates left in solution shows that all of the prominent compounds (I, II, V, VI, and VII) observed in the basic condensation appear in the acidic system. As would be expected, the general shape of the NMR patterns of these intermediate compounds is unchanged although there is some change in the chemical shift due to the change of solvent. For the methylenediphosphonate anion, it is seen that the protonation induced by going from the basic to the acidic medium leads to a 2-ppm downfield shift and a similar shift is observed for the terminal phosphorus atoms of II.

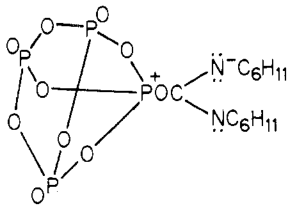
Full Condensation of Phosphoric Acids. The above evidence that methylenediphosphonic acid will undergo complete condensation to form the analog of the P_4O_{10} molecule having two oxygen bridges replaced by CH_2 groups rekindled our interest in trying to drive the condensation of simple orthophosphoric acid all the way to phosphorus pentoxide. Since we felt that this synthesis would be merely an example of the law of mass action, we worked to develop a procedure[21] for driving the reaction in the desired direction, as described below.

A number of different carbodiimides were tested for this purpose and it was found that the dicyclohexyl derivative (which is the reagent of choice for most of the biochemical condensations of phosphates) exhibited an advantageous combination of properties. First, it has a low melting point so that it can be used not only as a condensing agent but as a solvent as well. In addition, its hydration product crystallizes well and is essentially insoluble in the molten carbodiimide as well as in tetramethylurea. Although tetramethylurea is a good solvent for the highly ionized phosphates and molten carbodiimide is not, increasing condensation leads to a decrease in ionic character so that the carbodiimide concentration may be increased greatly as condensation proceeds.

Following this line of reasoning, we decided to start the condensation in tetramethylurea and then, in successive steps, to remove the crystalline dicyclohexylurea and concomitantly to increase the concentration of the carbodiimide. Thus, by employing five or more of these steps, simple orthophosphoric acid may be carried through the stages of (a) the tetrametaphosphoric acid followed by (b) the 1,5-μ-oxo-tetrametaphosphoric acid to (c) a structure which we have identified as the P_4O_{10} birdcage coordinated to a single carbodiimide, with the carbodiimide:phosphorus mole ratio being increased from 20:1 for the first step to 200:1 for the final step.

At the end of the reaction, we were able to show by use of ^{31}P NMR that all of the original phosphorus, except for a small amount lost with the urea precipitate, was present in the form of a single species exhibiting a pseudo-first-order doublet of relative area 3.0 centered at +59.5 ppm and a corresponding pseudo-first-order quartet of area 1.0 centered at +64.2 ppm. Homonuclear ^{31}P–^{31}P INDOR, with time averaging, showed that both of these multiplets originated from the same molecule. Since this resonance pattern appears much farther upfield than that of any other known phosphate resonance, we feel certain that the structure must be more fully condensed than any condensed phosphate previously studied in solution. This conclusion is based on the fact that going from the ortho to the end group to the middle group and then to the branch group in any phosphate system corresponds to a relatively large incremental upfield shift. Furthermore, for a group of a given functionality (e.g., a middle group) in a condensed phosphate, an increase in the functionality of the nearest-neighbor groups generally leads to an increase in the chemical shift of that group. All of these factors indicate that the high chemical shift of +60 ppm (as compared to the shift of +36 ppm for the branch group in the 1,5-μ-oxo-tetrametaphosphate anion in tetramethylurea or the shift of +49 ppm for the corresponding chloride derivative in the neat $POCl_3$–P_2O_5 system[22]) is associated with phosphate branch groups bonded only to other phosphate branch groups and thus probably occurring in a relatively small birdcage molecule. Following our usual practice in this field, the observed NMR spectrum was fitted theoretically to obtain the following NMR parameters for an a_3x molecule: δ_x 64.2 ppm, δ_a 59.5 ppm, $J_{a,x} = 18.0$ Hz, and $J_{a,a} < 6$ Hz. Note that in cyclic condensed phosphates we have found that coupling between chemically bonded "equivalent" groups is nontrivial (e.g., compound VI in a previous study[17]).

The only reasonable explanation for having three of the phosphorus atoms in this structure different from the fourth one is that the observed phosphorus molecule must have formed an adduct with the solvent; i.e., it has been "solvated" with the rate of exchange of the solvent molecules being sufficiently low so that the NMR technique was capable of observing the adduct. As expected, raising the temperature of the reaction mixture to promote exchange resulted in the broadening and eventual convergence of the two multiplets; however, we did not effect complete collapse of the multiplets into the sharp singlet anticipated for P_4O_{10} because of the increased solubility of the urea with rise in temperature and the sensitivity of the preparation to contamination by trace amounts of moisture. The only solvent molecule which has a suitable chemical structure for adding to a phosphoryl oxygen is the carbodiimide, and the lack of any detectable coupling between a phosphorus atom of the adduct and one or more hydrogen atoms is an indication that the coordination occurs at the central carbon atom of the attached carbodiimide. (Note that adducts of this type but involving far less condensed phosphates have often been postulated[1,2,5,6] as intermediates in carbodiimide-mediated phosphorylations, although no direct evidence has ever been presented for their existence.) We therefore, assign the chemical structure **1** to the compound giving the observed a_3x ^{31}P NMR spectrum.



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Attempts to isolate this new compound were consistently thwarted by contamination with trace moisture—a situation which is in accord with the assigned structure. In all cases, the isolate turned out to be a highly viscous ultraphosphoric acid, which appeared to be the same as the product obtained from analogous operations carried out with phosphorus pentoxide suspended in the same solvent. In both cases, the corresponding ^{31}P NMR spectra exhibited similar broad bands in the middle- and branch-group spectral regions.

Controlled hydrolysis (effected by pouring the solution of the fully condensed phosphate into vigorously agitated, aqueous 1 *M* triethylammonium bicarbonate at pH 7) led to the quantitative formation of tetrametaphosphate. The same results were obtained when very dry P_4O_{10} was similarly hydrolyzed. Another interesting piece of evidence supporting the assigned structure for this molecule is that dilution of the product solution with scrupulous anhydrous tetramethylurea containing some dissolved dicyclohexylurea caused a diminution in the NMR pattern centered at +60 ppm with a concomitant rise in the resonances attributable to 1,5-μ-oxo-tetrametaphosphoric acid, as would be anticipated from conversion of the urea into its carbodiimide according to the law of mass action.

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Registry No. Methylenediphosphonic acid, 1984-15-2; dicyclohexylcarbodiimide, 538-75-0; orthophosphoric acid, 7664-38-2.

References and Notes

(1) H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest", Wiley, New York, N.Y., 1961.
(2) M. Smith, J. G. Moffatt, and H. G. Khorana, *J. Am. Chem. Soc.*, **80**, 6204 (1958).
(3) M. Smith and H. G. Khorana, *J. Am. Chem. Soc.*, **80**, 1141 (1958).
(4) G. Weimann and H. G. Khorana, *J. Am. Chem. Soc.*, **84**, 4329 (1962).
(5) A. R. Todd, *Proc. Natl. Acad. Sci. U.S.A.*, **45**, 1389 (1959).

(6) F. A. Cramer and G. Weimann, *Chem. Ber.*, **94**, 966 (1961).
(7) T. C. Myers, K. Nakamura, and A. B. Danielzadeh, *J. Org. Chem.*, **30**, 1517 (1965).
(8) An exception may possibly be found in $CHCl_3$ in which P_4O_{10} is soluble to a few percent by weight [E. Hayek and E. Rhomberg, *Monatsh. Chem.*, **83**, 1318 (1952)]. However, P–O–P scission is quite possible.
(9) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).
(10) T. Glonek, J. R. Van Wazer, and T. C. Myers, *Bioinorg. Chem.*, **1**, 1 (1971).
(11) T. O. Henderson, T. Glonek, R. L. Hilderbrand, and T. C. Myers, *Arch. Biochem. Biophys.*, **149**, 484 (1972).
(12) T. Glonek, T. O. Henderson, A. W. Kruski, and A. M. Scanu, *Biochim. Biophys. Acta*, **348**, 155 (1974).
(13) T. Glonek, T. O. Henderson, R. L. Hilderbrand, and T. C. Myers, *Science*, **169**, 192 (1970).
(14) T. Glonek, R. A. Kleps, and T. C. Myers, *Science*, **185**, 352 (1974).
(15) T. Glonek, J. R. Van Wazer, R. A. Kleps, and T. C. Myers, *Inorg. Chem.*, **13**, 2337 (1974).
(16) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5** (1967).
(17) T. Glonek, J. R. Van Wazer, M. Mudgett, and T. C. Myers, *Inorg. Chem.*, **11**, 567 (1972).
(18) A. J. R. Costello, T. Glonek, T. C. Myers, and J. R. Van Wazer, *Inorg. Chem.*, **13**, 1225 (1974).
(19) W. E. Morgan, T. Glonek, and J. R. Van Wazer, *Inorg. Chem.*, **13**, 1832 (1974).
(20) T. Glonek, T. C. Myers, P. Z. Han, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **92**, 7214 (1970).
(21) T. Glonek, T. C. Myers, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **97**, 206 (1975).
(22) W. E. Morgan, T. Glonek, and J. R. Van Wazer, *Inorg. Chem.*, **13**, 1832 (1974).

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Thermochemical Investigation into the Lewis Acidity of the Boron Atom in Some Triaryloxyboranes

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Thermochemical measurements have shown that the Lewis acidity of the boron atom in a series of eight substituted triaryloxyboranes $B(OC_6H_4X)_3$ varies according to the electronic properties and position of the substituent. This is attributed to a variation in the basicity of the *internal* oxygen bases which participate in the intramolecular Lewis acid–base π interaction with the boron atom. For the systems studied the maximum variation amounts to 60 kJ mol^{-1} between the para-substituted cyano and methoxy compounds.

Introduction

The relative acidity of the boron atom in BL_3 compounds (L = H, halogen, alkyl, aryl, OR, or NR_2) has been of interest for some time. In these compounds the *internal* base in L participates in an intramolecular Lewis acid–base reaction and donates electron density into the empty p orbital of the boron atom by a $p\pi$–$p\pi$ mechanism. In the past this π stabilization or vertical reorganization energy[1] has been considered in thermodynamic cycles as a fixed quantity, characteristic of the acid and independent of the base.[2]

Drago[3] has shown that this concept of a constant reorganization energy for each Lewis acid is incorrect and that the extent of rearrangement of the acid is variable depending upon the strength of the bond formed with the *external* base and suggests that there is residual π bonding in the adducts. The mass spectral data of Lanthier and Millar on trimethylamine adducts of the boron halides support the idea of residual π bonding in the boron–halogen bonds in donor–acceptor complexes.[4] Shriver and Swanson[5] have obtained data, from B–N bond lengths and force constants in boron trifluoride and trichloride adducts of acetonitrile, that question the traditional idea of reorganization energies. It has also been shown, from a theoretical investigation into the mechanism of adduct formation of boron trifluoride and borane complexes, that these reactions can proceed without activation energy.[6]

In a real situation, therefore, the boron atom acidity is satisfied by electron donation from the *external* and *internal* bases. In this situation, where π bonds already exist and the possibility of σ-bond formation arises, it is to be expected that the energy of the π bonds will diminish as the molecule distorts to facilitate the σ-bond formation. This process will continue until maximum stabilization (minimum energy) of the whole system is achieved. The strength of the σ bond and the extent of the acid reorganization will depend on the basicity of the *external* base relative to the *internal* bases. Data on the magnitude of the interaction between boron Lewis acids and several *external* bases are available.[2b] In addition there are several theoretical calculations of π reorganization energies which for the boron halides give the order $BF_3 > BCl_3 > BBr_3 > BI_3$.[7] These values must now be considered to represent a maximum value for the intramolecular acid–base interaction. Lappert et al.[8] have shown, from extended Hückel calculations based on mass spectral data, that in the boron halides the π charge transfer from halogen to boron follows the order $BI_3 > BBr_3 > BCl_3 > BF_3$ and that the overall boron–halogen bond polarity is dominated by the σ charge drift from the boron to halogen. These two sequences are not incompatible. The results of other calculations agree with both sequences with the exception of BI_3.[1]

It would be of interest therefore to see to what extent the intramolecular π stabilization energy can be modified by manipulating the π basicity of the *internal* bases while keeping the *external* base constant. This will allow conclusions to be drawn about the importance of π stabilization energies in such systems. To do this requires a system where such variables as $B \rightarrow L$ σ charge drift, due to the different electronegativities of L, and steric and/or nonbonded electron repulsions, which may come into operation on adduct formation, are minimized. The only major variable has to be the π electron density on the internal bases. These criteria cannot be achieved when there is a total change of L in BL_3. If, however, the $p\pi$ electron basicity of the *internal* bases can be manipulated over a reasonable range without any major alteration to the system, it should be possible to obtain quantitative data that can be identified with the variation in π stabilization energy of the acid system under investigation. Furthermore some idea about the magnitude of the variation in reorganization energies of the acid in the general acid–base reaction (eq 1) is to be

$$\text{base} + BL_3 \rightarrow \text{base}\cdot BL_3 \qquad (1)$$

expected; here the basicity of the base varies over a wide range (amines, ethers, halide ions, etc.) as the acid is kept constant.