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Mixed Phosphorus(III)–Phosphorus(V) Oxide Chalconides

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Tetraphosphorus hexaoxide, P_4O_6, and tetraphosphorus heptaoxide, P_4O_7, were oxidized by reaction with P_4S_{10} or P_4Se_{10} to extend a class of adamantanoid structures based upon the P_4O_6 cage. The redistribution reactions of P_4O_{10} with P_4S_{10}, P_4O_6 with P_4O_{10}, P_4O_6 with $P_4O_6S_4$, and P_4O_6S with P_4Se_{10} are reported. The compounds P_4O_6S, $P_4O_6S_2$, $P_4O_6S_3$, $P_4O_6S_4$, P_4O_6Se, $P_4O_6Se_2$, $P_4O_6Se_3$, P_4O_6SSe, P_4O_7S, $P_4O_7S_2$, $P_4O_7S_3$, P_4O_7Se, P_4O_8, P_4O_8S, and $P_4O_8S_2$ were identified, and all were found to be structural derivatives of the P_4O_6 cage. Phosphorus-31 chemical shifts are compared and related to available structural information. The reaction of P_4O_7S to produce $P_4O_6S_2$ and P_4O_8 is also discussed. An improved preparation of P_4O_7 is presented.

Introduction

Recent studies of the molecule P_4O_6 have confirmed its tetrahedral tetradentate nonchelating ligative properties. These studies have shown the sequential ligation of the four phosphorus base sites to produce products of the type $P_4O_6(M)_n$, where $n = 1$–4 and M = $Ni(CO)_3$,[1] BH_3,[2–4] and $Fe(CO)_4$[5] (Figure 1). The four phosphorus(III) sites can also be oxidized by either oxygen or sulfur to yield respectively P_4O_{10} and $P_4O_6S_4$.[6] As demonstrated by structural studies, the integrity of the P_4O_6 cage is *maintained* during oxidation of either part or all of the phosphorus atoms in the compounds P_4O_8,[7,8] P_4O_9,[7,8] P_4O_{10},[7–9] and $P_4O_6S_4$[9] with the addition of exocyclic oxygen or sulfur atoms (Figure 1). Recently in our laboratories P_4O_7 was isolated[10] and was also found to be a structural derivative of P_4O_6. The compound P_4O_7 was found to react as a Lewis base with its remaining three trivalent phosphorus atoms toward metal carbonyls and boron trifluoride.[11] The study of the ligative ability of P_4O_7 indicated the possibility of forming mixed oxygen–chalconide oxidative derivatives of the P_4O_6 cage. This paper reports the oxidation of P_4O_6 and P_4O_7 to produce mixed phosphorus oxysulfides and oxyselenides.

Results and Discussion

The oxidation of the phosphorus cage molecule P_4O_6 by either P_4S_{10} or P_4Se_{10} occurs with the retention of the cage to produce the series of compounds $P_4O_6Y_n$, $n = 1$–4 for Y = S and $n = 1$–3 for Y = Se (Figure 1). The structure of these compounds can be confirmed by their ^{31}P NMR chemical shifts and coupling constants, which produce spin systems of the type $A_{4-n}M_n$ (Table I). Similarly, P_4O_7 (Figure 1b), which already contains one oxidized phosphorus atom, i.e., P=O, can be oxidized either by P_4S_{10} to produce chalconide derivatives of the type $P_4O_7Y_n$, $n = 1$–3, Y = S, or by P_4Se_{10} to produce P_4O_7Se. In the reactions studied, three other structural derivatives of P_4O_6 were also found: P_4O_8S and $P_4O_8S_2$, containing two oxygen atoms exocyclic to the cage and one and two sulfur atoms, respectively, and P_4O_6SSe, a mixed sulfide–selenide derivative.

These compounds further demonstrate the known tendency of phosphorus to maintain closo-type structures in simple molecular compounds.[12] These phosphorus oxysulfide and oxyselenide compounds are structurally identical with the very recently reported derivatives of another phosphorus cage molecule $P_4(NMe)_6$, for which the series $P_4(NMe)_6S_nO_{4-n}$, $n = 1$–3, was reported.[13] Previously only two phosphorus oxysulfides, $P_4O_6S_4$[6] and $P_4S_6O_4$,[14] and no oxyselenides have been reported. The compounds herein described represent the first reported molecular species that contain a P_4O_6 core with mixed substituents, i.e., oxygen, sulfur, and selenium, on the cage periphery.

The closo or cage structure of the compounds has been confirmed by their ^{31}P NMR spectra. The spectral interpretation is particularly simple because of the tetrahedral symmetry of P_4O_6 which leads to first-order spectra upon oxidative addition of oxygen and/or the chalconides sulfur and selenium exocyclic to the cage periphery. Also, no elements with a nuclear spin that would complicate the interpretation of coupling constants are involved.[15] The ^{31}P chemical shifts are typical[16] of the possible types of phosphorus atoms present: P(III) phosphite, phosphoryl P=O, thiophosphoryl P=S, and selenophosphoryl P=Se.

Synthesis of $(P_4O_6)S_n$, $n = 1$–4, and $(P_4O_6)Se_n$, $n = 1$–3. When P_4O_6 and P_4S_{10} were heated to reflux in toluene, after ca 0.5 h one sulfur atom was found to add to the cage to produce P_4O_6S, as monitored by ^{31}P NMR (Table I and Figure 1b). The reaction could be stopped at this point and filtered under an inert atmosphere to remove unreacted P_4S_{10}, with subsequent isolation of the product by sublimation. The disubstituted product $P_4O_6S_2$ was produced by increasing the ratio of P_4S_{10} to P_4O_6 and the reflux time. The $P_4O_6S_2$ formation was again monitored by ^{31}P NMR (Table I and Figure 1c), with isolation of the product being achieved in a similar fashion to that of P_4O_6S. Upon increase in the P_4S_{10} to P_4O_6 ratio and reaction time, $P_4O_6S_3$ and $P_4O_6S_4$ resulted (Table I and Figure 1d,e). If unsublimed P_4S_{10} was used (probably containing some water) in the reaction with P_4O_6, then $P_4O_7S_3$ and $P_4O_8S_2$ (Figure 1e) were also found, as monitored by ^{31}P NMR (Table I). We earlier reported that P_4O_7 is formed by heating P_4O_6 in ether solvents or in nonether solvents containing traces of water.[10] The products $P_4O_7S_3$ and $P_4O_8S_2$ were also found in the reaction between P_4O_7 and P_4S_{10} (vide infra). The probable source of $P_4O_7S_3$ and $P_4O_8S_2$ in the reaction of P_4O_6 with unsublimed P_4S_{10} is therefore from the decomposition of P_4O_6 to form P_4O_7 with subsequent reaction with P_4S_{10}.

A previous report[17] indicated that $P_4O_6S_4$ was formed by a sealed-tube reaction of P_4O_{10} with P_4S_{10} at 450 °C. Repetition of this experiment varying the ratio of P_4O_{10} to P_4S_{10} from 6:1 to 3:2 confirmed the formation of $P_4O_6S_4$. At lower ratios of P_4O_{10} to P_4S_{10}, the only phosphorus oxysulfide observed was $P_4O_6S_4$, whereas at higher ratios $P_4O_8S_2$ and $P_4O_7S_3$ were also observed. Attempts to produce P_4O_6S, $P_4O_6S_2$, or $P_4O_6S_3$ by the sealed-tube reaction of P_4O_{10} and P_4S_{10} in varying mole ratios were unsuccessful. Some $P_4O_6S_3$ was found, however, by NMR when $P_4O_6S_4$ was heated in the presence of Ph_3P, presumably formed by the removal of a S atom from $P_4O_6S_4$ by the Ph_3P.

Attempts to prepare P_4O_6 sulfides by the reaction of P_4O_6 with S_8 (in refluxing CS_2 or benzene or in a sealed tube at 130 °C) resulted in no reaction. Reaction of neat P_4O_6 with S_8 at 160 °C, as previously reported,[6,18] is violent, yielding a tarry residue from which $P_4O_6S_4$ can be extracted. Similarly the reaction between P_4O_6 and Ph_3PS (sealed tube, THF solvent, 130 °C for 24 h) resulted only in P_4O_7 plus unreacted starting compounds.

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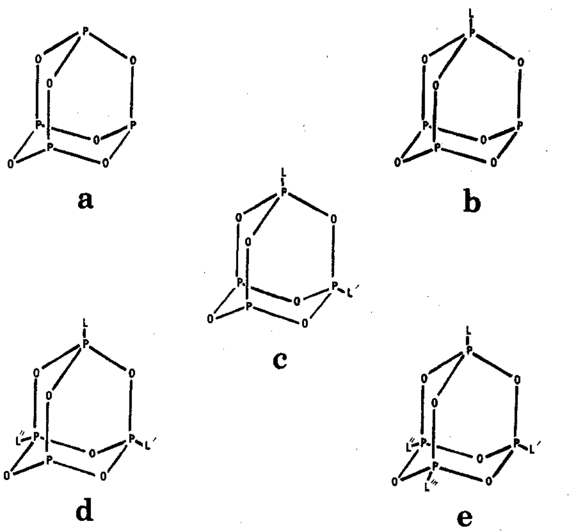

Figure 1. Structures for (a) P_4O_6, (b) P_4O_6L, with one P(III) atom oxidized or ligated, (c) P_4O_6LL', with two P(III) atoms oxidized or ligated, where L and L′ may be equal or different moieties, (d) $P_4O_6LL'L''$, with three P(III) atoms oxidized or ligated, where L, L′, and L″ may be equal or different, and (e) $P_4O_6LL'L''L'''$, with all four P(III) atoms oxidized or ligated, where L, L′, L″, and L‴ may be equal or different.

The series of compounds $P_4O_6Se_n$, $n = 1$–3, were formed by the reaction of P_4O_6 with purified P_4Se_{10} in refluxing *o*-xylene (Table I). As with the analogous sulfides, the number of selenium atoms adding to the cage, i.e., the degree of substitution, was controlled by the reflux time and by the ratio of P_4Se_{10} to P_4O_6. The failure to observe $P_4O_6Se_4$, analogous to $P_4O_6S_4$, apparently results from the fact that P_4Se_{10} is a poorer oxidizing agent than P_4S_{10}. The conditons required to add four Se atoms to the P_4O_6 cage are so vigorous that decomposition results first. One mixed sulfide–selenide P_4O_6SSe was also synthesized by the reaction of P_4O_6S with P_4Se_{10}.

Cage–Cage Redistribution Reactions. Riess and co-workers[13] have examined redistribution reactions of the sulfides $P_4(NMe)_6S_n$, $n = 1$–4, by heating, e.g., $P_4(NMe)_6$ with $P_4(NMe)_6S_4$, in a study of their relative thermodynamic stabilities. In contrast to the sulfides, the intermediate oxides, $P_4(NMe)_6O_n$, $n = 1$–3, were not observed to form by redistribution by heating $P_4(NMe)_6$ with $P_4(NMe)_6O_4$. Although we did not study similar redistributions in detail for our systems, we did find that when P_4O_6 and $P_4O_6S_4$ are heated, some P_4O_6S and $P_4O_6S_3$ were formed in addition to P_4O_7, which arose from the autoxidation of P_4O_6. In fact, some P_4O_7 was almost always observed in any reaction requiring heating of P_4O_6. When P_4O_6 was heated with P_4O_{10} in an effort to produce P_4O_7, P_4O_8, and P_4O_9 via redistribution, no P_4O_9 was observed although the heptaoxide and octaoxide were formed. Possibly P_4O_9, like P_4O_{10}, is too insoluble to be observed by ^{31}P NMR. Similarly P_4O_9S was never observed in any reactions, probably for solubility reasons.

Synthesis of P_4O_7 Oxygen, Sulfur, and Selenium Derivatives. An improved preparation for P_4O_7 was developed by using Ph_3PO. In earlier studies[10,11] P_4O_7 was synthesized by the pyrolysis of P_4O_6 in ether solvents or in nonether solvents such as benzene containing trace quantities of water. We now find that P_4O_7 can be prepared in THF at room temperature using Ph_3PO. The Ph_3PO apparently acts as a catalyst, since after the reaction only Ph_3PO is found rather than Ph_3P which would be the case if Ph_3PO were behaving as an oxidizing agent. Surprisingly, Me_3NO does not serve a similar purpose.[13]

Tetraphosphorus heptaoxide, P_4O_7, was also oxidized by either P_4S_{10} or P_4Se_{10} to produce a series of mixed phosphorus

Table I. ^{31}P NMR Data for P_4O_6 Oxide, Sulfide, and Selenide Derivatives in Benzene Solvent

compd	structure, figure no.	spin system[a]	chemical shift,[b] ppm				coupling const, Hz				
			P(III)	P(=O)	P(=S)	P(=Se)	$J_{P(III)-P(=O)}$	$J_{P(III)-P(=S)}$	$J_{P(III)-P(=Se)}$	$J_{P(=O)-P(=S)}$	$J_{P(=O)-P(=Se)}$
P_4O_7	1b	A_3M	−20.0	173.0			2.4				
P_4O_6S	1b	A_3M	−12.5		101.7			12.8			
P_4O_6Se	1b	A_3M	−11.0			100.2			17.5		
P_4O_8	1c	A_2M_2	−11.3	154.7			13.5				
P_4O_7S	1c	A_2MX	−11.0	160.0	88.1		9.5	0.7		46.5	
P_4O_7Se	1c	A_2MX	−10.5	163.9		84.0	9.9		5.0		51.0
$P_4O_6S_2$	1c	A_2M_2	−9.2		92.3			1.9			
P_4O_6SSe	1c	A_2MX	−7.8		97.7	92.2		3.0[c]	7.0[c]		
$P_4O_6Se_2$	1c	A_2M_2	−7.0			93.5			9.0		
P_4O_8S	1d	AM_2X	38.9	152.2	87.0		33.0	23.0		55.0	
$P_4O_7S_2$	1d	AM_2X	32.9	155.5	89.1		28.1	18.7		50.0	
$P_4O_6S_3$	1d	AM_3	27.5		91.8			14.3			
$P_4O_6Se_3$	1d	AM_3	24.1			93.0			4.0		
$P_4O_8S_2$	1e	M_2X_2		159.0	105.1					52.5	
$P_4O_7S_3$	1e	MX_3		159.5	103.2					48.0	
$P_4O_6S_4$	1e	M_4			103.4						

[a] All spectra were first order. In designating spin systems, A always refers to P(III) whereas M and X can each refer to P(=O), P(=S), or P(=Se). [b] Relative to P_4O_6. Upfield shifts are reported as positive. Chemical shifts can vary as much as several ppm as a function of concentration and solvent. [c] $J_{P(=S)-P(=Se)} = 50.5$ Hz.

oxysulfides or phosphorus oxyselenides, respectively. Thus, the reaction of P_4O_7 with P_4S_{10} in toluene in a sealed tube initially produced P_4O_7S (Figure 1c) as the major product. Additional heating yielded $P_4O_7S_2$ (Figure 1d) with the unexpected formation of P_4O_8 and $P_4O_6S_2$. Extended heating yielded, in addition to the above compounds, P_4O_8S, $P_4O_8S_2$, $P_4O_7S_3$, $P_4O_6S_3$, and $P_4O_6S_4$. Presumably the latter two compounds formed from the reaction of $P_4O_6S_2$ with P_4S_{10} (vide supra). Also noted by NMR after extensive heating was some tetraphosphorus trisulfide, P_4S_3, resulting as a reduction product of P_4S_{10} (the other phosphorus sulfides P_4S_5 and P_4S_7 are essentially insoluble and would not be observed by ^{31}P NMR). The reaction of P_4O_7 with P_4Se_{10} was also examined, although not as extensively as the reaction of P_4O_7 with P_4S_{10}. The products identified were P_4O_7Se, P_4O_8, and $P_4O_6Se_2$. Because of the extreme air sensitivity of the derivatives of P_4O_6 with both exocyclic oxygen and chalconide atoms and because of the mixture of products, these compounds were not isolated but were identified only by their ^{31}P NMR parameters (Table I). Thus P_4O_7S and P_4O_7Se yielded AM_2X spin patterns, and $P_4O_7S_2$ yielded an A_2MX ^{31}P spin pattern, while the fully oxidized $P_4O_7S_3$ yielded an A_3X pattern.

In the above reaction between P_4O_7 and P_4S_{10}, after the formation of P_4O_7S was noted, $P_4O_6S_2$ and P_4O_8 formation commenced. Since no P_4O_6S was observed at any time during the reaction, as monitored by ^{31}P NMR, it is tentatively concluded that a bimolecular exchange of exocyclic moieties between oxygen and sulfur occurred:

$$2P_4O_7S \xrightarrow{\Delta} P_4O_8 + P_4O_6S_2$$

Once $P_4O_6S_2$ was formed, further oxidation of it occurred more readily than oxidation of P_4O_7S or P_4O_8, as observed by the increased formation of $P_4O_6S_3$ and $P_4O_6S_4$ relative to that of $P_4O_7S_2$. At the termination of the reaction, the major observable phosphorus-containing compounds were $P_4O_6S_4$ and P_4S_3. Also found in the reaction mixture at the termination of the reaction were $P_4O_8S_2$ and $P_4O_7S_3$, as would be expected from the above reaction scheme. The latter two compounds were major components of the reaction of P_4O_{10} with P_4S_{10}.

A similar argument can be made for the reaction of P_4O_7 with P_4Se_{10}, where the observed products were P_4O_7Se, P_4O_8, and $P_4O_6Se_2$. Since at no time in the reaction was P_4O_6Se observed, the reaction $2P_4O_7Se \xrightarrow{\Delta} P_4O_6Se_2 + P_4O_8$ is proposed. As noted earlier, P_4Se_{10} is a poorer oxidizing agent than P_4S_{10}. Therefore, attempts to produce more highly oxidized species in the reaction yielded polymeric decomposition products.

The absence in this study of the observance of any compounds built upon a P_4S_6 cage indicates that reactions involving P_4S_{10} are more complicated than a simple exchange of exocyclic sulfur atoms. The degradation of the P_4S_{10} cage appears to occur with substitution of oxygen bridges for sufur bridges. It has been reported that the S—P═O linkage is unstable with respect to isomerization to O—P═S linkage for a series of thiosilylphosphoryl halides.[19]

^{31}P NMR. As well as being useful for the elucidation of the structures of these phosphorus closo compounds, the ^{31}P NMR spectra provide considerable insight into their bonding. In a quantum mechanical treatment, Riess and Van Wazer[20] found that, in P_4O_6 derivatives, the ^{31}P chemical shifts are related to the electronegativity of the Lewis acid complexing agent. Bond angle changes within the P_4O_6 cage that result upon coordination, as well as phosphorus d_π orbital occupation, are intimately related to the electronegativity of the Lewis acid complexing agent, despite the fact that these terms may be artificially separated. Thus, for an isostructural series, such as P_4O_6Y, it is not surprising that a linear relationship was found between the phosphorus(III) resonance and the electronegativity of the exocyclic Y moiety (Figure 2). This simple dependence possibly is indicative of the overall rigidity of the adamantoid structure such that any effect that obtains for the phosphorus(III) chemical shift upon varying the exocyclic atom can be viewed as an inductive one transmitted by the P(V)–O–P(III) linkage. Chemical support for this inductive effect can be found in the reaction of B_2H_6 and BF_3 with P_4O_6 or P_4O_7.[2,3,11] It was found that BF_3 coordinates with P_4O_7 but not with P_4O_6, while B_2H_6 will react with P_4O_6 but not with P_4O_7. The hard acid BF_3 should preferentially bond with the harder phosphorus cage compound P_4O_7, while the soft acid BH_3 should be expected to bond to the softer P_4O_6.[21] Qualitatively the phosphorus(III) lone pairs on P_4O_7 are less polarizable than those on P_4O_6, presumably due to the electron-withdrawing effect of the exocyclic oxygen on P_4O_7. Pertinent to the argument, it was also found that $P_4O_6S_2$ was more easily oxidized than P_4O_8 by P_4S_{10}. The partial charge on the phosphorus(V) atoms in $P_4O_6S_2$ should not be as great as the partial charge on the phosphorus(V) atoms in P_4O_8, due to the electronegativity difference between sulfur and oxygen. The more polarizable phosphorus(III) lone pairs in $P_4O_6S_2$ are therefore more easily oxidized.

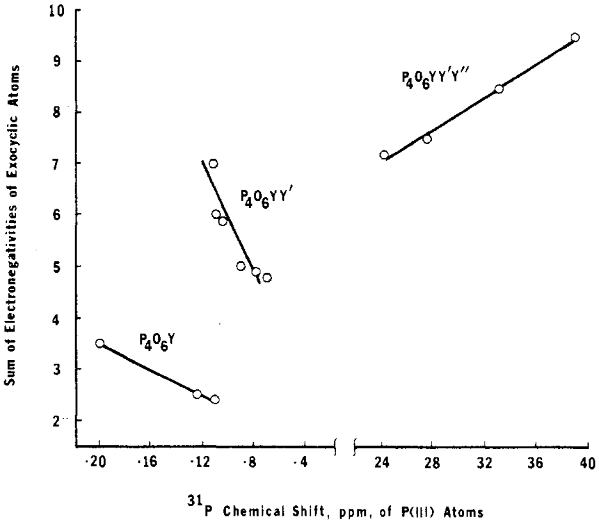

Figure 2. Plot of the sum of the Pauling electronegativities of the exocyclic substituents on a partially oxidized P_4O_6 cage vs. the ^{31}P NMR chemical shift of the nonoxidized P(III) atoms on the same molecule. The approximately linear relationship is shown for three series: P_4O_6Y (Figure 1b), P_4O_6YY' (Figure 1c), and $P_4O_6YY'Y''$ (Figure 1d).

A similar relationship between the phosphorus(III) resonance and the electronegativity of the exocyclic substituents obtains for the disubstituted series of compounds P_4O_8, $P_4O_6S_2$, $P_4O_6Se_2$, P_4O_7S, P_4O_7Se, and P_4O_6SSe. Figure 2 shows a plot of the P(III) resonance vs. the sum of the electronegativities of the exocyclic atoms. The relationship is approximately linear for the entire series, which encompasses the six molecules P_4O_7Y, Y = O, S, and Se, and P_4O_6YY', Y = S, Se and Y' = S, Se. For the trisubstituted compounds P_4O_8S, $P_4O_7S_2$, $P_4O_6S_3$, and $P_4O_6Se_3$ a linear relationship again was found between the phosphorus(III) resonance and the sum of the electronegativities of the exocyclic substituents, although the slope was opposite in sign. The apparent anomalies in the di- and trisubstituted compounds between electronegativity and chemical shift of the phosporus(III) resonance show the problems inherent with assuming that diamagnetic shielding will be the dominant term in ^{31}P chemical shifts, even in these highly constrained compounds. Even though a clear relationship exists between electronegativity and chemical shift for isostructural series of compounds (Figure 2), which is quite helpful in compound identification and even in prediction of chemical shifts of new compounds in a series, the magnitude and direction of relationship are very dependent upon other factors such as small bond angle changes and phosphorus d_π orbital occupation.

Prediction of phosphorus(V) chemical shifts is more difficult than for phosphorus(III) shifts for P_4O_6 derivatives. Quantum mechanical calculations indicate that the chemical shift of the coordinated phosphorus is dependent upon, in addition to other terms, the electronegativity of the complexing agent to both the first power and the second power, and these terms are opposite in sign.[20] The phosphoryl resonances all occur in the approximate range +150 to +170 ppm, the thiophosphoryl resonances in the range +88 to +150 ppm, and the selenophosphoryl resonances in the range +84 to +100 ppm.

The coupling constants in this work do not show an overall consistency based upon either substitution number or electronegativity but do show a generality corresponding to the oxidation state of the phosphorus atom in question. In general, the closer the phosphorus atoms are in oxidation state, the larger the coupling constant. Thus P_4O_8S has the largest coupling constant of 55.0 Hz for O=P—O—P=S, while P_4O_7S has the smallest observed coupling constant of 0.7 Hz for P(III)—O—P=S. The lack of coupling constant signs precludes any further instructive insight.

Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian Associates NMR Model XL-100-15 Fourier transform spectrometer. Chemical shifts for ^{31}P are reported relative to P_4O_6 as an internal standard or relative to internal P_4O_7 or $P_4O_6S_4$ referenced to external P_4O_6 (P_4O_7, −20.0 ppm (doublet), +173.0 ppm (quartet); $P_4O_6S_4$, +103.4 ppm). Downfield (shielded) shifts are recorded as negative values. IR spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer, and mass spectra were recorded on a Varian Matt Model 311 spectrometer. Elemental analyses were done by Chemalytics, Tempe, Ariz.

The manipulation of the air-sensitive compounds was carried out under a nitrogen atmosphere by using Schlenkware techniques in conjunction with either a helium-filled box equipped with a recirculating system or a static helium atmosphere box using sodium/potassium alloy as oxygen and water scavenger.[22] All solvents were reagent grade, dried either by distillation from CaH_2 or $LiAlH_4$ or by storage over CaH_2 for several days. Tetraphosphorus decasulfide and phosphorus pentaoxide were purchased from Fisher Chemical Co. Tetraphosphorus decaselenide was obtained from Research Organic/Inorganic Chemical Corp. Phosphorus pentaoxide was used as received, while P_4S_{10} and P_4Se_{10} were purified by first heating to ca. 100 °C under vacuum to remove volatile impurities, followed by sublimation at 250–300 °C. The suboxides P_4O_6, P_4O_7, and P_4O_8 were prepared according to literature procedures.[7,8,10,11]

Reactions. (a) Reaction of P_4O_6 with P_4S_{10}. To 50 mL of degassed, dry toluene in a three-necked flask were added under a N_2 blanket 0.6 mL (5.2 mmol) of P_4O_6 and 2.4 g (5.5 mmol) of purified P_4S_{10}. The mixture was heated to reflux (110 °C) for 30 min. Vigorous stirring was essential, as P_4S_{10} is insoluble in toluene. The solution was cooled to ambient temperature and filtered in an all-glass filtering system. The toluene was removed by vapor transfer at room temperature. The resultant white crystals were transferred into a sublimator in a drybox. The P_4O_6S was twice sublimed (0 °C cold finger, 10^{-5} torr) to yield clear, colorless crystals. Anal. Calcd for P_4O_6S: P, 49.17. Found: P, 50.48. The mass spectrum was very sensitive to spectrometer conditions, yielding a parent peak varying for 10–20% relative intensity: calcd for P_4O_6S, 251.83657; found, 251.83397. IR (cm^{-1}): 1006 (m), 986–940 (s), 895 (m), 850 (m), 687 (m), 663 (m), 642 (m), 626 (m), 528 (m), 515 (m), 415 (m). ^{31}P NMR parameters are given in Table I. If the above reaction was carried out in *o*-xylene by using 0.4 mL (3.5 mmol) of P_4O_6 and 2.3 g (5.2 mmol) of P_4S_{10} with heating to reflux (144 °C) for 20 min with purification as above, $P_4O_6S_2$ was isolated. The compound was identified by ^{31}P NMR. (Table I). Mass spectrum: calcd for $P_4O_6S_2$, 283.80914; found, 283.80864. If the above solution was refluxed for 5 h (instead of 20 min), sublimation at 60 °C yielded $P_4O_6S_3$ and $P_4O_6S_4$ with small amounts of $P_4O_6S_2$ (Table I). The tetrasulfide $P_4O_6S_4$ was identical with the product obtained from the reaction of P_4O_{10} and P_4S_{10} (vide infra). Mass spectra of the mixture indicated parent peaks for $P_4O_6S_2$, $P_4O_6S_3$, and $P_4O_6S_4$. In all of the above reactions, trace amounts of water in the solvent led to the production of P_4O_7 (Table I), with concomitant reaction of P_4O_7 with P_4S_{10} (vide infra).

(b) Reaction of P_4O_6 with S_8. When P_4O_6 and S_8 were refluxed in either CS_2 or C_6H_6 in an effort to produce P_4O_6S, $P_4O_6S_2$, $P_4O_6S_3$, and $P_4O_6S_4$, no reaction occurred. In a sealed tube at 130 °C, little reaction occurred between P_4O_6 and S_8. However, at 160 °C, a violent reaction occurred, leading to a tarry residue. A ^{31}P NMR spectrum of the extract indicated some $P_4O_6S_4$ was formed.

(c) Reaction of P_4O_{10} with P_4S_{10}. In a drybox, 1.09 g (7.65 mmol) of P_4O_{10} and 1.11 g (5.01 mmol) of P_4S_{10} were mixed in a mortar. The solid material was added to a Carius tube and sealed under vacuum. The contents were dispersed along the side of the tube, and the tube was placed in an oven at 450 °C for 8 h. The resulting solid was placed in a Soxhlet extractor with CS_2. The CS_2 was removed from the extract by vapor transfer, and the residue was sublimed (60 °C bath, 0 °C cold finger). The ^{31}P NMR and the mass spectra showed $P_4O_6S_4$. Higher ratios of P_4O_{10} to P_4S_{10} (6:1) were found to produce small quantities of $P_4O_7S_3$ and $P_4O_8S_2$ (Table I), in addition to $P_4O_6S_4$.

(d) Reaction of $P_4O_6S_4$ with Ph_3P. Some $P_4O_6S_4$ in benzene was added to Ph_3P in a cursory experiment to see if the Ph_3P would remove an S atom from $P_4O_6S_4$ to form $P_4O_6S_3$. A yellow precipitate formed immediately upon addition. A ^{31}P NMR of the solution indicated the presence of $P_4O_6S_3$ and $P_4O_6S_4$. The reaction was not further characterized. A similar reaction between $P_4O_6S_4$ and Hg yielded no observable $P_4O_6S_3$.

(e) Reaction of P_4O_6 with $P_4O_6S_4$. In a typical reaction approximately equimolar quantities of P_4O_6 and $P_4O_6S_4$ were introduced into an NMR tube in a drybox. The tube was transferred to a vacuum line, and benzene was vapor transferred into the tube. The tube was sealed off and removed from the line. The NMR tube was inverted and placed in an oven. As monitored both by visual means and by ^{31}P NMR spectroscopy, no reaction occurred until 130 °C. Heating at 130 °C for 1.5 h produced P_4O_6S and $P_4O_6S_3$ with some P_4O_6 and $P_4O_6S_4$ remaining. A small quantity of P_4O_7 was also observed.

(f) Reaction of P_4O_6 with Ph_3PS. In an attempt to produce P_4O_6S, equimolar quantities of P_4O_6 and sublimed Ph_3PS were dissolved in THF and placed in a sealed tube. The tube was heated at 130 °C for 24 h. A ^{31}P NMR spectrum showed no P_4O_6S, but some P_4O_7 was observed from the decomposition of P_4O_6.

(g) Reaction of P_4O_6 with P_4Se_{10}. Under an inert atmosphere 7.6 g (8.3 mmol) of P_4Se_{10} was mixed with 1.0 mL (8.8 mmol) of P_4O_6 in *o*-xylene or mesitylene. The mixture was refluxed for 6 h. The product was purified in the same manner as P_4O_6S. The ^{31}P NMR (Table I) indicated P_4O_6Se. Higher mole ratios of P_4Se_{10} to P_4O_6 (8.2:6.2 mmol) heated at reflux for 9 h produced approximately equimolar quantities of P_4O_6Se and $P_4O_6Se_2$ with a small quantity of $P_4O_6Se_3$. Further heating produced insoluble, polymeric material.

(h) Reaction of P_4O_6S with P_4Se_{10}. In an NMR tube equimolar quantities of P_4O_6S and P_4Se_{10} were mixed in *o*-xylene. The tube was sealed and heated at 140 °C for 1 h. A ^{31}P NMR spectrum showed peaks corresponding to P_4O_6S, P_4O_7, P_4O_7S, $P_4O_6S_2$, and P_4O_6SSe. No isolation was attempted.

(i) Reaction of P_4O_6 with P_4O_{10}. Approximately 2 g (7.0 mmol) of P_4O_{10} was added to 0.4 mL (3.5 mmol) of P_4O_6 in dry mesitylene. Refluxing for 2 h resulted in no reaction, so 1 drop of water was added to catalyze the reaction. Refluxing for 3 h yielded a small amount of P_4O_7 in addition to unreacted P_4O_6, as monitored by ^{31}P NMR spectroscopy. Refluxing for a total of 16 h resulted in almost total consumption of P_4O_6, a large quantity of P_4O_7, and a small quantity of P_4O_8. Further refluxing (34 h, total) showed no P_4O_6 and about equal quantities of P_4O_7 and P_4O_8. Continued refluxing for several days resulted in a progressive decrease of P_4O_7 and P_4O_8, with no other compounds being observable by ^{31}P NMR spectroscopy.

(j) Reaction of P_4O_6 with Ph_3PO. One milliliter (8.8 mmol) of P_4O_6 and 2.5 g (8.8 mmol) of Ph_3PO were dissolved in 5 mL of dry THF. After the mixture was stirred at ambient temperature for about 8 h, a considerable quantity of yellow precipitate formed; ^{31}P NMR spectroscopy showed a large quantity of P_4O_7 with no P_4O_6 remaining. The reaction was filtered in an all-glass system. The THF was removed by vapor transfer, and the resulting solid was extracted with 10 mL of benzene. The benzene was removed by vapor transfer, and the solid was sublimed (60 °C bath, 0 °C cold finger, 10^{-5} torr) to yield

P_4O_7. Analysis of the THF-soluble, benzene-insoluble solid showed Ph_3PO and no Ph_3P. The reaction was also attempted in benzene and diethyl ether, and no reaction occurred at room temperature over a several-day period. Similarly, no reaction occurred between P_4O_6 and Me_3NO in THF at room temperature.

(k) Reaction of P_4O_7 with P_4S_{10}. In a typical reaction 0.3 g (1.3 mmol) of P_4O_7 and 0.8 g (1.8 mmol) of P_4S_{10} were added to an NMR tube in a drybox. The tube was placed on a vacuum line, and about 1.0 mL of toluene was transferred to the tube which was then sealed. The tube was inverted, transferring all of the liquid and solid to the sealed end of the tube. The tube was then heated to 125 °C for about 1 h until all of the P_4O_7 had reacted. After all of the P_4O_7 had been consumed, the temperature was increased to 150 °C. The reaction was monitored by ^{31}P NMR spectroscopy every 2 h. Initially after 1 h of heating, the major product was P_4O_7S, with 2 h of additional heating producing $P_4O_7S_2$ with some P_4O_8 and $P_4O_6S_2$. Further oxidation of $P_4O_6S_2$ occurred more readily than P_4O_7S or P_4O_8, as observed by the large quantities of $P_4O_6S_3$ and $P_4O_6S_4$. Extended heating for 30–45 h yielded P_4O_8S, $P_4O_8S_2$, $P_4O_7S_3$, $P_4O_6S_3$, and primarily $P_4O_6S_4$. Some P_4S_3 was also observed.

(l) Reaction of P_4O_7 with P_4Se_{10}. The same procedure was used as in the above reaction of P_4O_7 with P_4S_{10}. The products identified by NMR spectroscopy after 2 h of heating at 145 °C were P_4O_7Se, P_4O_8, and $P_4O_6Se_2$. Due to the extreme sensitivity and the mixture of products, no compound isolation was achieved.

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Registry No. P_4O_7, 55230-51-8; P_4O_6S, 70983-15-2; P_4O_6Se, 70983-16-3; P_4O_8, 70983-17-4; P_4O_7S, 70983-18-5; P_4O_7Se, 70983-19-6; $P_4O_6S_2$, 70983-20-9; P_4O_6SSe, 70983-21-0; $P_4O_6Se_2$, 70983-22-1; P_4O_8S, 70983-23-2; $P_4O_7S_2$, 70983-24-3; $P_4O_6S_3$, 70983-25-4; $P_4O_6Se_3$, 70983-26-5; $P_4O_8S_2$, 70983-27-6; $P_4O_7S_3$, 70983-28-7; $P_4O_6S_4$, 15780-31-1; P_4O_6, 10248-58-5; P_4S_{10}, 15857-57-5; S_8, 10544-50-0; P_4O_{10}, 16752-60-6; Ph_3P, 603-35-0; P_4Se_{10}, 62493-85-0; Ph_3PO, 791-28-6.

References and Notes

(1) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, 2166 (1966).
(2) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, 2339 (1966).
(3) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **89**, 851 (1967).
(4) G. Kodama and H. Kondo, *J. Am. Chem. Soc.*, **88**, 2045 (1966).
(5) M. L. Walker and J. L. Mills, *Inorg. Chem.*, **14**, 2438 (1975).
(6) T. E. Thorpe and A. E. Tutton, *J. Chem. Soc.*, **59**, 1023 (1891).
(7) D. Heinz, *Z. Anorg. Allg. Chem.*, **336**, 137 (1965).
(8) D. Heinz, H. Rienitz, and D. Rodeck, *Z. Anorg. Allg. Chem.*, **383**, 12 (1972).
(9) D. E. C. Corbridge, *Top. Phosphorus Chem.*, **3**, 57 (1966).
(10) M. L. Walker and J. L. Mills, *Synth. React. Inorg. Met.-Org. Chem.*, **5**, 29 (1975).
(11) M. L. Walker and J. L. Mills, *Inorg. Chem.*, **16**, 3033 (1977).
(12) J. R. Van Wazer, "Phosphorus and Its Compounds", Interscience, New York, 1958; D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", Elsevier, London, 1974; D. A. Armitage, "Inorganic Rings and Cages", Arnold, New York, 1972.
(13) F. Casabianca, A. A. Pinkerton, and J. G. Riess, *Inorg. Chem.*, **16**, 864 (1977).
(14) E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 5585 (1964). The structure of this molecule was proposed to consist of a P_4S_6 cage with four exocyclic oxygens. Elemental analysis was the only evidence given for the compound. In light of our studies and those of others (M. L. Walker and A. H. Cowley, unpublished results) who have been unable to repeat the preparation, the proposed structure of $P_4S_6O_4$ is unlikely.
(15) Although ^{77}Se has a nuclear spin of $^1/_2$, it is not present in sufficient concentations (7.58% natural abundance) to normally result in observable coupling.
(16) J. R. Van Wazer and J. H. Letcher, *Top. Phosphorus Chem.*, **5**, 169 (1967).
(17) J. C. Pernert and J. H. Brown, *Chem. Eng. News*, **27**, 2143 (1949).
(18) H. Gerding and H. Van Brederode, *Recl. Trav. Chim. Pays-Bas*, **64**, 183 (1945).
(19) R. G. Cavell, R. D. Leary, and A. J. Tomlinson, *Inorg. Chem.*, **11**, 2573, 2578 (1972).
(20) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
(21) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(22) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969.

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Thermodynamics of the $AlCl_4^-$ Ion by Lattice-Energy Studies

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Using the recently obtained crystal structure data for lithium, sodium, potassium, cesium, and ammonium tetrachloroaluminates, we have computed the total lattice energies by using the method of Jenkins and Pratt. $\Delta H_f°(AlCl_4^-(g))$ is estimated to be -1188 kJ mol^{-1}, and the halide ion affinities for the processes $AlCl_3(ss) + Cl^-(g) \rightarrow AlCl_4^-(g)$ are determined, where (ss) represents (c), (l), and (g).

This study concerns the crystal structures and associated thermochemical data of tetrachloroaluminate salts. From a knowledge of the crystal structures of $LiAlCl_4$, $NaAlCl_4$, $KAlCl_4$, $CsAlCl_4$, and NH_4AlCl_4, thermodynamic parameters, "basic" radii, and charge distribution for the $AlCl_4^-$ anion are obtained which confirm in part and extend the results of previous studies. Studies on these systems are of inherent interest because of the importance[1,2] of tetrahalometalate salts as electrolytes,[3] as heat-exchange fluids in nuclear reactors,[4] and as catalysts in organic systems and because of their thermal stability and use as media for the preparation of unusual oxidation states. The study of the effective charges in tetrahalometalate ions has received attention in connection with the estimation of bonding energies in conjunction with the ESCA technique[5] and NQR spectroscopy.[6]

Crystal Structure Data

Table I gives the lattice parameters and structural details concerning the tetrachloroaluminates for the alkali metal salts (except rubidium) and the ammonium salt.

All the tetrachloroaluminates crystallize with four molecules per unit cell ($Z = 4$). The structure of $LiAlCl_4$ is given in ref 7. The $NaAlCl_4$ structure of Baenziger[8] has been refined by Scheinert and Weiss[6] and refined also in this laboratory[9] with an improved accuracy. $KAlCl_4$[10] has been determined to have two molecular formulas in the asymmetric unit.

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