Organophosphorus Detergents*

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Summary

A survey on the use of organophosphorus compounds in the detergent field is given. In particular, the use of organophosphorus compounds as surface active agents, lime soap dispersants and deflocculating agents, stabilizers of bleaching solutions, solubilizers of water in water immiscible solvents, bacteriostates, corrosion inhibitors and sequestrants and builders is described. Methods for the syntheses of the individual compounds are also reported.

Introduction

Whereas phosphates and polyphosphates have been used since a long time in the detergent field, the application of organophosphorus compounds for this purpose has been developed only in the passed ten years. Organophosphorus compounds have been claimed to be useful as surface active agents, lime soap dispersants and deflocculating agents, stabilizers of bleaching solution, solubilizers of water in water immiscible solvents, bacteriostates, corrosion inhibitors, sequestrants and builders. It is the purpose of this review to summarize the known uses of organophosphorus compounds in the detergent field and to discuss the preparation of the individual compounds.

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Data and Discussion

A. Organophosphorus Surfactants

1. General Discussion

As the earliest surfactants (other than soap) the sulfated oils were extensively used by the textile industry. Therefore it seems reasonable to assume that simple substitution of a phosphoric acid or oxide for sulfuric acid might provide better materials since phosphates can be good water conditioners, whereas the sulfated oils were unstable towards hard water. An early attempt at reacting condensed phosphoric acid with castor oil gave a polyphosphoric acid ester which, when neutralized with ammonia was said to be useful because of high wetting power and great stability to hard water[2]. Other less expensive phosphating agents have been used and some improvements in hard-water resistance for the phosphated compounds appear to exist as shown in Table A-1, but even this leaves much to be desired in comparison with really effective surfactants. Other phosphate derivatives have been evaluated and the most effective surfactants are those made from mixed long-chain alcohols but the choice of organic radicals must be carefully made to preserve water solubility[8].

The results in Table A-1 deserve some comment. Phosphated castor oil appears to be a superior product when compared to the corresponding sulfation product

Table A-1. Surfactant Properties of Organophosphorus Compounds

Compound	Draves wetting time in sec of a 25% solution	Detergency (0.2% at 300 ppm water hardness)	Calcium salt value (100 = excellent)	Surface tension dynes/cm concentration 0.25%	Literature
Phosphates:					
Phosphated castor oil	180	70	42	39	
Turkey red oil	180	18	3	44	
Loralkyl phosphate	180	67	2	50	
Lorol metaphosphate	180	70	100	47	1
Octyl phosphate	13.8	39	3	45	
Octyl sulfate	180	23	100	36	
Na-octyl-tripolyphosphate	15.5	67	24	26	
Phosphonic acid salts:					
Dodecylbenzene sodium phosphonate	180	85	1	39	
Dodecylbenzene sodium sulfonate	4.0	83	16	37	
Kerosene sodium phosphonate	14	88	26	36	
Lauryl sodium phosphonate	67	85	15	36	
Nonyl sodium phosphonate	180	84	14	30	
Oleyl sodium phosphonate		119	17	36	
Phosphinates:					
Dodecylbenzene sodium phosphinate	58	54	5	37	

Table 1-A continued

	Surface tension in dynes/cm Concentration in % 0.1	0.0007	Literature
Substituted phosphonic acids and salts:			
$C_{16}H_{26}CH(OH)P(O)(OH)_2$ (*p*H 4, 50°)	32		3a
(*p*H 11, 50°)	50		
R $SCH_2P(O)(OH)_2$ R = C_{13} to C_{17}		40–46	3b
$CH_3(CH_2)_nC(=O)NHCH_2P(O)(OH)_2$			
n = 10	60		3c
n = 12	54		
n = 14	46		
n = 16	37		
$C_{12}H_{25}C_6H_4P(O)(OH)_2$ *p*H 3.3	25		3d
7.5	47		
12.0	42		

	Concentration in % 1	0.1	0.01	0.001	0.0005	Literature
Phosphonic acid monoesters:						
Capryl-P(O)OH(OEt)	26.3					4
Lauryl-P(O)OH(OEt)	31.4					4
Phosphonic acid diesters:						
$C_{12}H_{25}P(O)(OCH_3)_2$		26.6	27.3	45.5		3
$C_{14}H_{29}P(O)(OCH_3)_2$		25.3	25.4	40.6		3
$C_{12}H_{25}P(O)(OEt)_2$		27.7	27.8	28.7		3
Diphosphonic acids:						
$CH_2[PO_3Na_2]_2$			50.6	52.3		5
$C_8H_{17}CH[PO_3Na_2]_2$			49.2	32.3		5
$C_{12}H_{25}CH[PO_3Na_2]_2$			28.4	32.6		5
$C_7H_{15}C(OH)[PO_3H_2]_2$	28.0					4
$C_{11}H_{23}C(OH)[PO_3H_2]_2$	29.1					4
Alkylamino bis(methylphosphonic acid) trisodium salts:						
$RN(CH_2PO_3Na_2)(CH_2PO_3HNa)$						
R = CH_3				60	72	6
C_6H_{13}				64	62	
Cyclo-C_6H_{11}				61	61	
C_8H_{17}				44	56	
$C_{10}H_{21}$				40	44	
$C_{12}H_{25}$				39	44	
$C_{14}H_{29}$				38	44	
$C_{16}H_{33}$				34	36	
$C_{18}H_{35}$				44	44	
Phosphine oxides:						
$(CH_3)_2n\text{-}C_{12}H_{25}PO$		25.3	25.3			7
$(CH_3)_2(n\text{-}C_{14}H_{29})PO$		27.6	27.0			
$(n\text{-}C_4H_9)_2(n\text{-}C_{12}H_{25})PO$			31.2			
$(C_2H_5)_2n\text{-}C_{12}H_{25}PO$		22.3	34.0			
Phosphine sulfides:						
$(CH_3)_2(n\text{-}C_{14}H_{29})PS$			35.5			
$Et_2(n\text{-}C_{12}H_{25})PS$			36.1			7
$Et_2(n\text{-}C_8H_{17})PS$			40.0			

(Turkey red oil) but is more expensive. The effect of proper choice of hydrophobe chain lenght of optimum solubility with increased surface activity is shown by the octyl phosphate/sulfate comparison. Both are quite stable to hard water, neither possesses effective detergent properties and, although the phosphate is a better wetting agent it has a higher surface tension than the sulfate. Comparison of octyl *ortho*-phosphate with the octyl tripolyphosphate shows improvement in the latter for detergency, surface tension and hard water stability. Phosphonation has given a product essentially equivalent to dodecylbenzene sodium sulfonate but the phosphonate is more expensive which has prevented its adoption. Oleyl sodium phosphonate is one of the very few organic phosphorus compounds to have outstanding detergency, but the surfactancy is not completely satisfactory. The surfactancy is markedly improved when the half-ester of phosphonates such as O-ethylesters of capryl or laurylphosphonic acids are used[4] (see Table A-1). Substituted diphosphonic acids[4, 5] and alkylamino-bis-(methylphosphonic acid) trisodium salts[6] do not seem to have as good surfactant properties as phosphonic acids and their esters, but show good properties as sequestering agents for Ca, Fe, and the like, ions[4, 5], and also deflocculating and dispersing properties[5, 6] (Table 2). In addition of not only being excellent surfactants, phosphonate diesters of general formula $RP(O)(OR')_2$ ($R = C_{12}$ to C_{14} alkyl, $R' = CH_3$ or C_2H_5) are also effective bacteriostates[3]. The same property is shared by phosphine oxides[9, 7] and phosphine sulfides[7] of general formula $RR'R''P{=}O$ (or S) ($R = C_{10}$ to C_{18} alkyl, R', $R'' = C_1$ to C_3 alkyl). Unsymmetrical tertiary phosphine oxides seem to be the most effective surfactants so far found amongst the organophosphorus compounds. Furthermore, the phosphine oxides, and in particular C_{12}–C_{14} alkyl-, dimethyl- or diethylphosphine oxides show highly desirable properties such as excellent detergency also in cold water, alkaline earth soap solubilization characteristics, resistance to hydrolysis, high thermal stability, low degree of hydroscopicity and bacteriostatic activity[9]. Heavy-duty laundering compositions are obtained which have outstanding effectiveness in both cool and hot water detergency when these phosphine oxides are combined with water soluble inorganic alkaline builder salts or organic alkaline sequestrant builder salts in the ratio of 1 : 1 to 1 : 10. It has been claimed that in the cool water detergency effectiveness these phosphine oxides are much more effective than soap, such as coconut oil soap, and are also more effective than commonly used laundering active detergents such as alkylbenzenesulfonates[9]. Only the high cost of preparation has so far prevented commercialization of these phosphine oxides.

2. *Preparation of Some Phosphorus Containing Surfactants*

a) Phosphates:

One of the oldest and cheapest methods for the synthesis of mixtures of primary and secondary phosphates is the reaction of hydroxycompounds with P_2O_5[10, 11].

$$3\,ROH + P_2O_5 \rightarrow (RO)P(O)(OH)_2 + (RO)_2P(O)OH$$

$$(RO)_3PO + P_2O_5 \rightarrow 3\,ROPO_2 \xrightarrow{H_2O} 3\,ROP(O)(OH)_2$$

$$(RO)_2P(O)Cl + H_2O \rightarrow (RO)_2P(O)OH$$

The pentaoctyl tripolyphosphate is obtained in the same way.

$$5\,C_8H_{17}OH + 3\,P_2O_5 \rightarrow (C_8H_{17})_5H_5(P_3O_{10})_2$$

b) Phosphonates:

Phosphonates are obtained either by the Michaelis-Becker or Arbuzov reaction[10, 11].

$$(RO)_2PONa + RX \rightarrow (RO)_2P(O)R + NaX$$

$$(RO)_3P + R'X \rightarrow (RO)_2P(O)R' + RX$$

c) Phosphine oxides and sulfides:

Although several methods exist for the preparation of phosphine oxides[10, 11] and sulfides[13] good synthetic procedures for unsymmetrical phosphine oxides and sulfides have been developed only recently.

Phosphine Oxides:

$$3\,R_2NPCl_2 + 2\,Al(CH_3)_3 \rightarrow 3\,R_2NP(CH_3)_2 \xrightarrow[-R_2NH]{+C_{12}H_{25}OH} (CH_3)_2POC_{12}H_{25} \xrightarrow{\Delta/RX} (CH_3)_2P(=O)C_{12}H_{25}$$ 13

$$C_{12}H_{25}PH_2 + 2\,CH_3I \rightarrow [C_{12}H_{25}P(CH_3)_2]\cdot HI \xrightarrow{OH^-/H_2O_2} C_{12}H_{25}P(=O)(CH_3)_2$$ 14

$$C_{12}H_{25}PH_2 + 3\,CH_3Cl \rightarrow [C_{12}H_{25}P(CH_3)_3]Cl \xrightarrow[NaOH]{solid} C_{12}H_{25}P(=O)(CH_3)_2$$ 14,15

$$(RO)_2P(=O)H + 3\,MgXR \rightarrow R_2P(=O)MgX \xrightarrow{R'X} R_2R'P{=}O$$ 16,17,18

$$(CH_3)_2P(=O)H + \text{dodecene} \rightarrow C_{12}H_{25}P(=O)(CH_3)_2$$

$$[C_{12}H_{25}P(CH_3)_2C_6H_5]Cl + NaOH \rightarrow C_{12}H_{25}P(O)(CH_3)_2 + C_6H_6$$ 19

Table 2. Deflocculating Properties of Some Organophosphorus Compounds

Compound	Apparent Viscosity (Cp) at 300 rpm. Stormer at indicated weight percent of deflocculation on a dry clay basis				
$RN[CH_2P(O)(ONa)_2][CH_2P(O)(ONa)OH]$ concentration	0	0.1	0.15	0.2	Ref.
$R = CH_3$	Plastic	180	180	180	6
C_4H_9	Plastic	220	210	200	6
C_6H_{13}	Plastic	220	210	200	6
C_8H_{17}	Plastic	180	180	180	6
$C_{14}H_{29}$	Plastic	380	370	390	6
$C_{18}H_{35}$	Plastic	1400	1000	1100	6
$RCH[PO_3Na_2]_2$					
$R = H$	Plastic	230	230	230	5
C_7H_{15}	Plastic	270	370	270	5
$C_{12}H_{25}$	Plastic	350	350	350	5
Sodium tripolyphosphate	Plastic	180	180	180	5

Phosphine sulfides:

$$(CH_3)_2PNR_2 + H_2S \rightarrow (CH_3)_2\overset{S}{\overset{\|}{P}}—H \xrightarrow[\text{AIBN}]{\text{tetradecene}} C_{14}H_{29}\overset{S}{\overset{\|}{P}}(CH_3)_2 \quad [20]$$

$$(CH_3)_2P(S)Cl + RMgBr \rightarrow (CH_3)_2P(S)R + MgClBr \quad [12]$$

$$(CH_3)_2PC_{12}H_{25} + S \rightarrow (CH_3)_2P(S)C_{12}H_{25} \quad [12]$$

B. Organophosphorus Compounds as Lime Soap Dispersants and Deflocculating Agents

1. *General Discussion*

When straight soaps are used in hard water, insoluble soaps form gummy, flocculant precipitates until the calcium and magnesium ions are essentially used up. It is only then that foaming is observed. When a good lime soap dispersant together with a soap regenerating agent is added foaming ability is immediately observed and the "bath-tub ring" is not formed. Trisodium phosphate and condensed phosphates act as lime-soap dispersants and regenerants because of their ability to complex metal ions[1]. In the past few years it has been found that substituted methylenediphosphonic acids of the type[21,5,22]

$$H_2O_3P\overset{X}{\underset{Y}{C}}PO_3H_2$$

X, Y = Br, Cl, H, OH, NH_2, C_7 to C_{20} alkyl, at least one of X or Y being other than hydrogen

alkylaminodi(methylenephosphonic acids)[6]

$$RN(CH_2PO_3H_2)_2$$

and organoaminopoly(methylphosphonic acids),

$$(H_2O_3PCH_2)_2N(CH_2)_xN(CH_2PO_3H_2)_2 \quad [22,23]$$

exhibit good properties as lime soap dispersants, deflocculating agents and complexing agents (Table 2). In comparison with the condensed phosphates they have the advantage of not hydrolyzing in aqueous solution. It has also been claimed that dimethyldodecylphosphine oxide is an outstanding foam stabilizer and lime soap dispersant[9,19]. Some results are tabulated in Table 2.

2. *Preparation of Some Organophosphorus Compounds Effective as Lime Soap Dispersants and Deflocculating Agents*

Methylenediphosphonates are readily obtained by an Arbuzov reaction from tri-isopropylphosphite and CH_2Br_2[24]. Halogenation, or alkylation of methylenediphosphonates yields the substituted derivatives which on hydrolysis yield the corresponding acids

$$CH_2Br_2 + 2\,P(OPr\text{-}iso)_3 \rightarrow (iso\text{-}PrO)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{P}}(O—Pr\text{-}iso)_2 \quad [24]$$

$$(RO)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{P}}(OR)_2 + K \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}CHK\overset{O}{\overset{\|}{P}}OR \xrightarrow{RX} (RO)_2\overset{O}{\overset{\|}{P}}CHR\overset{O}{\overset{\|}{P}}(OR)_2 \quad [25,26,21]$$

$$(RO)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{P}}(OR)_2 + Br_2 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}CHBr\overset{O}{\overset{\|}{P}}(OR_2) \quad [21,26]$$

$$(RO)_2\overset{O}{\overset{\|}{P}}CHR\overset{O}{\overset{\|}{P}}(OR)_2 + 4\,HCl \rightarrow H_2O_3PCHRPO_3H_2 + 4\,RCl$$

α-Aminomethylphosphonic acids and aminopolymethylphosphonic acids are readily prepared by a Mannich type reaction with *ortho*-phosphorous acid[27] or directly from white phosphorus and N-hydroxymethyl dialkylamines[28].

$$RNH_2 + 2\,CH_2O + 2\,HP(O)(OH)_2 \rightarrow RN[CH_2PO_3H_2]_2 + 2\,H_2O \quad [27]$$

$$H_2NCH_2CH_2NH_2 + 4\,CH_2O + 4\,H_3PO_3 \rightarrow [H_2O_3PCH_2]_2NCH_2CH_2N[PO_3H_2]_2 \quad [27]$$

$$2\,P_4 + 20\,R_2NCH_2OH \rightarrow R_2NCH_2PO_3H_2 + 2\,(R_2NCH_2)_2PO_2H + 5\,(R_2NCH_2)_3P{=}O + 8\,H_2O \quad [28]$$

C. Stabilization of Bleaching Solutions by Organophosphorus Compounds

1. General

Although bleaching processes are widely used in the textile industry beaching compositions are universally used in laundering and frequently are accepted for their sanitizing value. Bleaching is usually achieved by either using hypochlorite or percompounds such as sodium or hydrogen peroxides of other persalts. In order to keep up the effectiveness of the bath, stabilizers such as sodium silicates or tetrasodium pyrophosphate are added.

Alkylenediphosphonic acid and salts of formula $H_2O_3P(CXY)_nPO_3H_2$ ($n = 1$ to 10, X = H or lower alkyl, Y = H, OH, NH_2, lower alkyl)[29,30] and aminotri (lower alkylidenephosphonic acids) or their salts of formula $N(CXYPO_3H_2)_3$[31] are effective of not only stabilizing peroxide bleaching solutions but also chlorine bleaching solution. The mechanism of stabilization of these compounds is believed to involve sequestration of heavy-metal cations which catalyze bath decomposition. Perhydrates of hydroxyalkylidene diphosphonic acids, $H_2O_3PC(OH)RPO_3H_2 \cdot xH_2O_2$ have been said to be storable in solid form without addition of further stabilizers over a long period without appreciable loss of oxygen[32]; they also have the property of sequestering heavy-metal cations in solution.

Table 3. Stabilization of Bleaching Solutions by Organophosphorus Compounds

Compound added (concentration in %)		Time in min	Residual H_2O_2 present after indicated time (in %)
Control (no stabilizing agent)		15	0
$N(CH_2PO_3H_2)_3$	0.001	20	98
		40	13
	0.002	20	100
		40	91
	0.01	20	100
		40	99
		60	98

			Residual chlorine-releasing agent (in %)	
			Na-hypochlorite	K-dichloroisocyanurate
$N(CH_2COONa)_3 \cdot H_2O$	3.0 (*p*H 10)	180	0.7	
$Na_2O_3PCH_2PO_3Na_2$	3.0 (*p*H 10)	180	98.6	76.2
$Na_2O_3PC(OH)CH_3PO_3Na_2$	3.0 (*p*H 10)	180	92.0	30.4

2. Preparation of Phosphorus Containing Stabilizers for Bleaching Solutions

The preparation of methylenediphosphonic acids has been described under section B2. Nitrilotri (methylenephosphonic acid) may be prepared by the following three routes

$$N[CH_2P(O)(OR)_2]_3 + 6\,HCl \rightarrow N(CH_2PO_3H_2)_3 + 6\,RCl \qquad {}^{33}$$

$$NH_3 + 3\,ClCH_2PH(O)OH \rightarrow N(CH_2PH(O)OH)_3 \xrightarrow{H_2O_2} N(CH_2PO_3H_2)_3 \qquad {}^{34}$$

$$NH_3 + 3\,CH_2O + 3\,H_3PO_3 \rightarrow N(CH_2PO_3H_2)_3 \qquad {}^{27}$$

D. Solubilization of Water in Water Immiscible Solvents by Organophosphorus Compounds

The ability of some organophosphorus compounds to impart a solubilizing action to water in water immiscible solvents such as hexane, CCl_4 or perchloroethylene, renders them useful as dry cleaning agents, particularly if they also show surfactancy properties.

Table 4. Gram Water Dissolved in 50 ml Hexane Containing 3 Grams of the Compound Shown

Compound	Gram H_2O dissolved
$C_{16}H_{33}N[CH_2P(O)(OC_2H_5)_2]_2$	3.0
$C_{12}H_{25}N[CH_2P(O)(OC_2H_5)_2]_2$	1.0
$C_8H_{17}N[CH_2P(O)(OC_2H_5)_2]_2$	0.7
iso-$C_4H_9N[CH_2P(O)(OC_2H_5)_2]_2$	Several drops
$CH_3N[CH_2P(O)(OC_2H_5)_2]_2$	0.0
	Gram water dissolved in 50 ml hexane containing 25 ml of the esters shown
$C_7H_{15}CH[P(O)(OC_2H_5)_2]_2$	2.5
$C_{12}H_{25}CH[P(O)(OC_2H_5)_2]_2$	12.5

The preparation of these compounds has been discussed in previous sections.

E. Bacteriostatic Properties of Some Organophosphorus Compounds

Detergents of themselves are not effective in preventing or arresting the growth or action of micro-organisms such as the *Staphylococcus aureus*. Thus, when such action is desired as is always in the detergent field, bacteriostatic agents must be incorporated. However, none

Table 5. Bacteriostatic Properties of Organophosphorus Compounds

Compound	Concentration (in ppm) required to stop multiplication of *Staphylococcus aureus*	Ref.
$C_{12}H_{25}P(O)(OC_2H_5)_2$	1 to 20	3
$C_{12}H_{25}P(O)(CH_3)_2$	17.5 to 19	8
$C_{14}H_{29}P(O)(CH_3)_2$	10	7
$C_8H_{17}P(S)(C_2H_5)_2$	10	7
$C_{12}H_{25}P(S)(C_2H_5)_2$	10	7

of the known bacteriostatic agents aids in the cleansing action. Therefore the finding that some highly active phosphorus containing surfactants also exhibit bacteriostatic properties is of importance. Among the compounds tested diethyldodecylphosphonate[3] some unsymmetrical tert. phosphine oxides[7,9] and unsymmetrical tert. phosphine sulfides[7] exhibited the highest activity. The results are shown in Table 5.

F. Organophosphorus Containing Corrosion Inhibitors

In order to reduce corrosion of metals and erosion of vitreous enamel surfaces corrosion inhibitors such as sodium silicate are added to the detergent composition. Some organophosphorus compounds have also been found useful for this purpose and in particular phosphonic acids such as the half-ester of caprylphosphonic acid, hydroxyalkylidenediphosphonic acids, $RC(OH)[PO_3H_2]_2$ [4] and phenylphosphinic acid $C_6H_5P(O)H(OH)$ have been said to be highly effective as corrosion inhibitors.

G. Organophosphorus Containing Sequestrants and Builders

1. General

The use of builders to improve detergency levels of synthetic detergents is well known. The exact behaviour and mechanics of how builders perform their function has never been fully explained, however[1]. This may be due in part to the complex nature of detergency itself and the number of factors which are involved. Among the many properties of built detergency systems on which builder materials are thought to have some effect are: stabilization of solid soil suspensions, ability to soften water, prevention of discoloration of clothes by iron, emulsification of solid particles, peptization of gums and solid particles of soil, rate of wetting of oily cloth by water, solubilization of water insoluble materials, foaming characteristics of washing solutions, neutralization of acid soil, surface activity of the aqueous detergent solution and complexing and peptization of inorganic constituents.

The major effects of the polyphate builders appear to be directly attributed to their ability to soften water. Since sodium tripolyphosphate hydrolyzes slowly in aqueous solution it is not suitable for liquid detergent formulations; therefore mainly sodium or potassium pyrophosphates are used as builders in these formulations. In recent years several organophosphorus compounds have been found which show outstanding sequestering ability not only for Ca- and Mg-ions but also for many other metal ions, and are therefore excellent detergent builders.

Since they are stable towards hydrolysis they may also be used in liquid detergent formulations. Among the many organophosphorus compounds, claimed to be useful for this purpose, methylene and substituted methylenediphosphonic acids of formula $H_2O_3PCXYPO_3H_2$ (X, Y = H, R, OH, Cl, Br, NH_2[35, 36, 37, 21, 30]) some polyphosphonic acids[50,51], nitrilotri(methylene-phosphonic acid) $N(CH_2PO_3H_2)_3$[27, 38, 39, 40], ethylenediaminetetra-(methylenephosphonic acid),

$$[H_2O_3PCH_2]_2NCH_2CH_2N[CH_2PO_3H_2]_2$$ [41, 42]*,

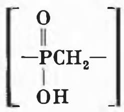
bis(phosphonylmethyl)phosphinic acid

$$[H_2O_3]PCH_2]_2PO_2H$$ [43],

tris(phosphonylmethyl)phosphine oxide

$$[H_2O_3PCH_2]_3PO$$ [44]

and a polyphosphinic acid,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have shown outstanding properties as sequestering agents. The results are summarized in Tables 6 to 9.

The results in Table 6 indicate that methylene and substituted methylenediphosphonic acids are better complexing agents than pyrophosphates. The stability constants for the Ca-complexes decrease, however, rapidly with increasing chain length between the two end-phosphonate groups.

Table 6. Dissociation Constants for Ca- and Mg-Complexes of Organophosphorus Containing Complexing Agents, Containing two Phosphorus Atoms (at 25 °C)

Compound	Ionic strength	$-\log \beta CaL$	$-\log \beta MgL$	Ref.
$P_2O_7^{-4}$	0.1	5.39		45
$O_3PNHPO_3^{-4}$	0.1	5.36		40
$O_3PCXYPO_3^{-4}$				
X = Y = H	0.1	6.0		36
	0.5	4.70	5.78	47
X = CH_3, Y = H	0.5	5.21	6.26	47
X = Y = CH_3	0.5	6.33	6.83	47
X = CH_3, Y = OH	0.5	5.74	6.39	47
	0.1	7.09		40
X = CH_3, Y = NH_2	0.1	6.71		
$O_3PCH_2CH_2PO_3^{-4}$	0.1	2.8	2.9	36

The values of the Ca-dissociation constants of complexing agents containing three phosphorus atoms decrease in the order expected upon considering the distance between the phosphorus atoms (Table 7).

* The subject of "organophosphorus Complexones" has recently been reviewed[42a].

Table 7. Dissociation Constants for Ca-Complexes of Organophosphorus Compounds Containing Three Phosphorus Atoms (at 25 °C)

Compound	Ionic strength	$-\log \beta$CaL	Ref.
$\left(O_3PO\overset{O}{\underset{O}{P}}OPO_3\right)^{-5}$	0.1	6.41	45
$\left(O_3PNH\overset{O}{\underset{O}{P}}NHPO_3\right)^{-5}$	0.1	6.74	46
$\left(O_3PCH_2\overset{O}{\underset{O}{P}}CH_2PO_3\right)^{-5}$	0.1	6.87	40

Table 8. Dissociation Constants for Ca- and Mg-Complexes of $X(CH_2CO_2H)_n(CH_2PO_3H_2)_{3-n}$; (X = N, N–O, P–O) (at 25 °C). $n = 0$ to 3

Compound	Ionic strength	$-\log \beta$CaL	$-\log \beta$MgL	Ref.
$N(CH_2CO_2H)_3$	0.1	6.41 [a]	5.41	48,40
$N(CH_2CO_2H)_2(CH_2PO_3H_2)$	0.1	7.18	6.28	48
$N(CH_2CO_2H)(CH_2PO_3H_2)_2$	0.1	6.17	–	42
$N(CH_2PO_3H_2)_3$	1.0	6.68	6.49	38
$ON(CH_2PO_3H_2)_3$	1.0	5.69	8.29	39
$OP(CH_2PO_3H_2)_3$	0.1	6.83 [b]	–	40
$ON(CH_2CO_2H)_3$	0.1	2.46	2.83	39
$(H_2O_3PCH_2)_2NCH_2CH_2N(CH_2PO_3H_2)_2$	0.1	5.74	–	42

a: $-\log \beta Ca_2L = 3.40$; *b*: $-\log \beta Ca_2L = 5.70$.

Table 9. Dissociation Constants of Ca-Complexes of Polymeric Phosphorus Containing Complexing Agents (0.1 M Ionic Strength at 25 °C)

Compound		$-\log \beta$Cal	Moles of phosphorus per bond Ca ion	Ref.
$\left[-\overset{O}{\underset{O}{P}}O\overset{O}{\underset{O}{P}}-\right]_n^{-2}$ Na⁺	$n = 3$	6.80	–	45
$\left[-\overset{O}{\underset{O}{P}}CH_2\overset{O}{\underset{O}{P}}O-\right]_n^{-2}$ Na⁺	$n \sim 5$	7.21	3.9	40
$\left[-\overset{O}{\underset{O}{P}}CH_2\overset{O}{\underset{O}{P}}CH_2\right]_n^{-2}$ TMA⁺	$n \sim 5$	7.38	4.2	40

Thus the Ca-complex of bis(phosphonylmethyl)-phosphinic acid is more stable than that of diiminotriphosphate which in turn is more stable than that of tripolyphosphate. Since, however, the electronegativity of the groups $-CH_2-$, $-NH-$, $-O-$ increases in the same manner as the distance between the atoms, it is not possible to indicate which of these phenomena are most important in determining the Ca-complexing ability[40].

The calcium complexing behaviour of the nitrilomethylenphosphonic acid series and the corresponding P-analogs illustrates an important feature of these phosphonates which differenciates them from their carboxyl analogs (Table 8). Ca-complex formation by the phosphonic acid derivatives is less sensitive to the bridging substituents.

Thus the stability constant of the Ca-complex drops upon oxidation of nitrilotri(methylenephosphonic acid) to nitrilotri(methylenephosphonic acid) N-oxide from 6.68 only to 5.69, whereas that of nitrilotri(acetic acid) upon oxidation to nitrilotri(acetic acid) N-oxide decreases from 6.41 to 2.46 (Table 8). This suggests that binding of Ca- and Mg-ions in compounds containing the $NCH_2PO_3^{2-}$-moiety is principally by the phosphonate group with little or no interaction by the tertiary nitrogen[38]. The most striking feature is the ability of tris-(dihydroxyphosphonylmethyl) phosphine oxide (II) to form Ca_2L-complexes under conditions where nitrilotri-(methylenephosphonic acid) does not[40] (Table 8).

And finally in comparing the dissociation constants of calcium-complexes of polymeric phosphorus containing complexing agents one again observes an order which is expected upon considering the distance between the phosphorus atoms (Table 9). Thus the Ca-complex of the polyphosphinic acid is more stable than that of the polyphosphonic acid, which in turn is more stable than that of the polyphosphoric acid (Table 9).

2. *Preparation*

The preparation of methylene- and substituted methylene diphosphonic acids (section B2) and of nitrilotri-(methylenephosphonic acid) (section C2) has been described previously.

Hydroxy- and amino-ethylidenediphosphonic acid are obtained by the following routes:

$$CH_3COOH + 2\,PCl_3 \xrightarrow{H_2O} H_2O_3PC(OH)(CH_3)PO_3H_2 \quad {}^{37}$$

$$(CH_3CO)_2O + 2\,H_3PO_3 \longrightarrow H_2O_3PC(OH)(CH_3)PO_3H_2 \quad {}^{37}$$

$$CH_2{=}C{=}O + 2\,H_3PO_3 \longrightarrow H_2O_3PC(OH)(CH_3)PO_3H_2 \quad {}^{37a}$$

$$P + CH_3COOH + O_2 \xrightarrow{80°} H_2O_3PC(OH)(CH_3)PO_3H_2 \quad {}^{49}$$

$$RCN + 2\,PCl_3 \xrightarrow{H_2O} RC(NH_2)(PO_3H_2)_2 \quad {}^{30}$$

Hydrolysis of bis(phosphonylmethyl)phosphinates and tris (phosphonylmethyl) phosphine oxides, which are obtained by the ARBUZOV reaction, with concentrated HCl yields the corresponding acids.

$$(HOCH_2)_2P(O)OH + 3\,SOCl_2 \rightarrow (ClCH_2)_2P(O)Cl$$

$$\xrightarrow{ROH} (ClCH_2)_2P(O)OR \xrightarrow{2\,P(OR)_3} [(RO)_2(O)PCH_2]_2P(O)OR$$

$$\xrightarrow{HCl} (H_2O_3PCH_2)_2PO_2H \quad {}^{43}$$

and

$$(HOCH_2)_3P{=}O + PCl_5 \rightarrow (ClCH_2)_3P{=}O$$

$$\xrightarrow{3\,(RO)_3P} [(RO)_2(O)PCH_2]_3P{=}O \xrightarrow{HCl} [H_2O_3PCH_2]_3P{=}O \qquad 44$$

Some polyphosphonic acids, also claimed to be useful as Ca-sequestering agents, were synthesized by the following routes:

$$H_2O_3PCH_2COOH + H_3PO_3 + PCl_3 \rightarrow H_2O_3PCH_2\overset{\displaystyle OH}{\overset{|}{C}}(PO_3H_2)_2 \qquad 50$$

$$2[(RO)_2(O)P]_2CHNa + CH_2Cl_2 \xrightarrow{toluene} [(R_2O_3P)_2CH]_2CH_2$$

$$\xrightarrow{HCl} [H_2O_3P]_2CHCH_2CH[PO_3H_2]_2 \qquad 51$$

And finally a polyphosphinic acid is also obtained by an Arbuzov rearrangement from chloromethylphosphonites:

$$ClCH_2PCl_2 + 2\,ROH \xrightarrow{R_3N} ClCH_2P(OR)_2$$

$$\xrightarrow{\Delta} ClCH_2\underset{OR}{\overset{O}{P}}[CH_2\underset{OR}{\overset{O}{P}}]_x CH_2P(OR)_2$$

$$\xrightarrow{O_2/HCl} (ClCH_2)(HO_2)P[CH_2PO_2H]_x CH_2PO_3H_2 \quad x \sim 9 \qquad 7$$

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References

1. J. R. Van Wazer, *Phosphorus and its Compounds,* Vol. II, Interscience, New York 1961.
2. G. S. Ranshaw, *Chem. Age 43* (1940) 51.
3. S. J. Fitch and R. R. Irani, U.S. Pat. 3.312.623 (1967).
   a) Y. Okamoto and H. Sakurai, *Kogyo Kagaku Zasshi 70* (1967) 1603; *Chem. Abstr. 68* (1968) 22018 t.
   b) K. Horiuchi, Y. Okamoto and H. Sakurai, *Kogyo Kagaku Zasshi 70* (1967) 173; *Chem. Abstr. 67* (1967) 100197 w.
   c) Y. Okamoto, T. Katakama and H. Sakurai, *Kogyo Kagaku Zasshi 70* (1967) 604; *Chem. Abstr. 67* (1967) 82242 a.
   d) Y. Okamoto, T. Nitta and H. Sakurai, *Kogyo Kagaku Zasshi 70* (1967) 1393; *Chem. Abstr. 68* (1968) 29794 b.
4. B. Blaser, H. G. Germscheid and K. H. Worms, DBP 1 148 552 (1963).
5. S. J. Fitch and R. R. Irani, U.S. Pat. 3.299.123 (1967).
6. R. R. Irani and K. Moedritzer, U.S. Pat. 3.344.077 (1967).
7. L. Maier, unpublished results.
8. L. Light, *Chem. Age 43* (1940) 55.
9. J. T. Yoke III and R. G. Lauphlin, U.S. Pat. 3.304.263 (1967); Belg. Pat. 615204 (1962).
10. G. M. Kosolapoff, *Organophosphorus Compounds,* John Wiley & Sons, 1950.
11. K. Sasse in Houben-Weyl, Band XII/1 and 2, Phosphorverbindungen, Verlag Thieme, Stuttgart 1964.
12. L. Maier, in *Topics in Phosphorus Chemistry,* Interscience, New York 1965, Vol. 2, p. 43.
13. L. Maier, *Helv. Chim. Acta 47* (1964) 2134.
14. H. R. Hays, *J. Org. Chem. 31* (1966) 3817.
15. H. R. Hays and R. G. Laughin, *J. Org. Chem. 32* (1967) 1060.
16. T. H. Siddall and M. A. Davies, *J. Chem. Eng. Data 10* (1965) 303.
17. J. J. Richard and C. V. Banks, *J. Org. Chem. 28* (1963) 123.
18. I. M. Downie and G. Morris, *J. Chem. Soc. 1965,* 5771.
19. H. M. Priestley, *J. Chem. Eng. Data 12* (1967) 618.
20. L. Maier, *Helv. Chim. Acta 49* (1966) 1249.
21. Procter & Gamble Co., Brit. Pat. 1.026.366 (1966).
22. H. J. Schlüssler, DAS 1252838 (1967).
23. R. R. Irani and K. Moedritzer, U.S. Pat. 3.298.956 (1967).
24. C. H. Roy, U.S. Pat. 3.251.907 (1966).
25. G. M. Kosolapoff, *J. Amer. Chem. Soc. 75* (1953) 1500.
26. O. T. Quimby, J. D. Curry, D. A. Nicholson, J. B. Prentice and C. H. Roy, *J. Organomet. Chem. 13* (1968) 199.
27. K. Moedritzer and R. R. Irani, *J. Org. Chem. 31* (1966) 1603.
28. L. Maier, *Helv. Chem. Acta 50* (1967) 1723; *ibid. 51* (1968) 1608.
29. M. Crutchfield and R. R. Irani, U.S. Pat. 3.297.578 (1967).
30. B. Blaser, H. G. Germscheid and K. H. Worms, DAS 1171401 (1964).
31. R. R. Irani, U.S. Pat. 3.234.140 (1966).
32. J. Schiefer, F. Weldes and K. H. Worms, DAS 1133726 (1962).
33. K. A. Petrov, F. L. Maklyaev and N. K. Bliznuk, *J. Gen. Chem.* USSR *29* (1959) 587.
34. E. H. Uhing and A. D. F. Toy, U.S. Pat. 3.160.632 (1964).
35. G. Schwarzenbach and J. Zurc, *Mh. Chem. 81* (1950) 202.
36. R. R. Irani and K. Moedritzer, *J. Physic. Chem. 66* (1962) 1349.
37. B. Blaser, H. Germscheid and K. Worms, Belg. Pat. 619.620 (1962); H. Germscheid and J. Schiefer, Canad. Pat. 701.850 (1965)
37. a) J. K Dyer, U.S. Pat. 3.666.675 (1968); *Chem. Abstr. 68* (1968) 105 362 b.
38. R. P. Carter, R. L. Carroll and R. R. Irani, *Inorg. Chem. 6* (1967) 939.
39. R. P. Carter, M. M. Crutchfield and R. R. Irani, *Inorg. Chem. 6* (1967) 943.
40. C. F. Callis, A. F. Kerst and J. W. Lyons, in press.
41. R. R. Irani, U.S. Pat. 3.234.124 (1966).
42. S. Westerback, K. S. Rajan and A. E. Martell, *J. Amer. Chem. Soc. 87* (1965) 2567.
42. a) M. I. Kabachnik, T. Ya. Medved', N. M. Dyatlova and M. V. Rudomino, *Usp. Khim. 37* (1968) 1161 (English translation).
43. L. Maier, *Angew. Chem. 80* (1968) 400, *Angew. Chem. Int. Ed. 7* (1968) 384; *Helv. Chim. Acta 52* (1969) 827.
44. L. Maier, *Angew. Chem. 80* (1968) 401, *Angew. Chem. Int. Ed. 7* (1968) 385; *Helv. Chim. Acta 52* (1969) 858.
45. R. R. Irani and C. F. Callis, *J. Physic. Chem. 64* (1960) 1398.
46. R. R. Irani and C. F. Callis, *J. Physic. Chem. 65* (1961) 296.
47. R. L. Carroll and R. R. Irani, *J. Inorg. Nucl. Chem. 30* (1968) 2971.
48. G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta 32* (1949) 1175.
49. Procter & Gamble Co., Neth. Pat. 6.610.762 (1967).
50. O. T. Quimby, U.S. Pat. 3.400.148 (1968).
51. O. T. Quimby, U.S. Pat. 3.400.176 (1968).