

699. *Determination of Association of Several Organophosphorus Acids.*

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The determination of the apparent molecular weights of representatives of the various families of organophosphorus acids in naphthalene was performed. It was shown that the substances that possess "true" acidic properties display association, probably by hydrogen-bonding; substances lacking acidic properties are monomeric. Acids of type $R \cdot PO_2H_2$ form trimeric aggregates; acids of type $R \cdot PO_3H_2$ form polymers of variable magnitude; acids of type R_2PO_2H form dimeric aggregates.

THERE is a significant lack in the chemical literature of knowledge about the states of aggregation of the acids of phosphorus which bear one or two organic radicals bound to the phosphorus atom. In order to interpret the physical and the chemical behaviour of the various families of such compounds, it was necessary first to secure some information concerning the probable molecular status of these substances in solution. The most elementary approach to the problem, of course, is the cryoscopic procedure.

Preliminary data obtained with benzene solutions of some dialkyl phosphites, with phenylphosphonous acid ($Ph \cdot PHO \cdot OH$), and with the mono-*n*-butyl ester of the acid have been reported elsewhere (*J. Amer. Chem. Soc.*, 1950, in the press). Further investigation confirmed the results secured with the model compounds mentioned above and was extended to other representatives. It was found, at very early stages of the investigation, that none of the common solvents that melt in the vicinity of room temperature provides a sufficient range of solubility for proper investigation of the compounds in question; naphthalene was therefore used. It was realized that the necessarily high temperature in such determinations might cause complete monomerization of any aggregates that could exist at substantially room temperature; however, even at temperatures around 80° the various aggregates were found to exist in substantially the same state as had been found in model experiments at low temperature.

A simple apparatus (see Experimental section) was constructed for these determinations and the device should be fully applicable to similar determinations with other materials of moderately high melting point.

The determinations of the cryoscopic molecular weights of a number of aromatic phosphonous acids indicated clearly that even at 80° these substances tend to approach the trimeric state. A

progressive increase of concentration of these substances in the naphthalene produces an asymptotic approach of the cryoscopic molecular weight to that of a trimer. Obviously, the effects of dilution and of the relatively high temperature cause some dissociation, but, even at the lowest concentrations used, the results are rather close to those expected of trimers. It is reasonable to assume that such an aggregate is cyclic, retaining its form by hydrogen bonds between the oxygen atoms. The bond undoubtedly involves the hydrogen of the one existing hydroxyl function on the one hand and the "singular" oxygen of the adjacent molecule on the other. The results obtained with the other series of phosphorus derivatives seem to preclude the possibility of the hydrogen bond involving the hydrogen attached to phosphorus in the commonly accepted formulation, $R\cdot PHO\cdot OH$. The aliphatic members of this series would have made a useful addition to our study, but all are liquids, the purity of which is dubious.

It is of interest that the trimeric, probably cyclic, aggregation of phosphonous acids is reflected very well in their solubilities. All these substances are at best sparingly soluble in water, but dissolve more or less readily in non-polar solvents. Elevated temperatures are necessary in many cases, it is true, but all of these acids recrystallize from benzene.

Only one example of the type $R_2P\cdot OH$ was investigated, as this ($R = p\text{-Me}_2N\cdot C_6H_4$) is the only known phosphinous acid. As might have been expected, this substance, lacking a true acid function, was found to be a monomer, as were the dialkyl phosphites, $(RO)_2\cdot P\cdot OH$.

Acids of type $R\cdot PO_3H_2$ (phosphonic acids), which have two acidic functions, presented a rather different picture. The aromatic members proved to be essentially insoluble in non-polar solvents and, except with the parent substance, phenylphosphonic acid, no satisfactory results could be obtained even with naphthalene as the solvent. The minute freezing-point depressions obtained at the limited concentrations possible were worthless. The aliphatic members were, however, satisfactorily soluble and the results obtained with them and some not very accurate results with the less soluble benzene derivative clearly indicated a progressive rise of apparent molecular weight with increase of concentration. The size of the aggregate goes beyond that of a hexamer for the more concentrated solutions, and no definite limiting size could be established. The apparent formation of a linear polymeric aggregate goes hand in hand with the relatively high solubility of the members of this family in water and the relatively poor solubility in non-polar solvents.

The acids of type $R_2PO\cdot OH$ (phosphonous acids) were generally readily soluble in naphthalene, the sole exceptions being the di-*o*-methoxyphenyl and bis-*p*-dimethylaminophenyl compounds which were too insoluble. These acids, resembling as they do the carboxylic acids in the constitution of their acidic function, were found to resemble the monocarboxylic acids also in their association. They were clearly dimeric. The reason for the hydrocarbon-insolubility of the *o*-methoxyphenyl member is not clear, since the existence of chelation with the methoxy-oxygen should have enhanced rather than depressed the solubility.

In conclusion, two statements appear to be justified by our results. The secondary esters of phosphorous acid, *i.e.*, $(RO)_2P\cdot OH$, are not associated in benzene or naphthalene. Consequently, if any hydrogen bonding is possible in compounds with a $P\cdot OH$ (or $O\cdot P\cdot H$) function, it is so weak as to be completely destroyed by dissolution even in cold benzene. Recent determinations of the parachor (Arbuzov and Vinogradova, *Doklady Akad. Nauk. S.S.S.R.*, 1946, **54**, 787; 1947, **55**, 31) and the Raman shift (Arbuzov, Batuev, and Vinogradova, *ibid.*, 1946, **54**, 599) for dialkyl phosphites led to the supposition of dimeric aggregation of these esters. Our results indicate that such an effect must occur only to a very slight extent, if at all. The second conclusion is that, apparently, the very tenacious aggregation of all phosphorus acids which have true acid functions explains the existence of very sparingly soluble "acid" salts which these acids form on partial neutralization.

[*Added in proof.*] After the manuscript had been submitted for publication, it came to our attention that Arbuzov and Vinogradova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1950, **72**, 695) reported the cryoscopically-determined molecular weights of several dialkyl phosphites. They found that when extremely concentrated solutions (in benzene) are used (freezing-point depressions of 16–20°), the calculated molecular weights tend to rise from monomeric value. However, it is questionable whether the concentrations used are at all significant, because of the obvious departure from the dilute-solution state and consequent inapplicability of the usual formulæ.

EXPERIMENTAL.

Apparatus.—The apparatus which served admirably for cryoscopic determinations with naphthalene as solvent was assembled from readily available components. The usual Beckmann-type freezing-point vessel, with a side-arm for sample introduction, was wound on its outside with two separate windings

of Nichrome wire, and the outer glass jacket was firmly slid over the winding, keeping it in place. The upper winding, located above the side-arm, consisted of ten turns of 1.5 ohms-per-foot wire and served to prevent sublimation into the upper part of apparatus. The lower winding, located at the bottom half of the vessel, consisted of ten turns of 3-ohms-per-foot wire and served as the source of added heat for re-melting the mixture for repeated determinations without disturbance of the assembly. A conventional differential thermometer and a motor-driven loop-shaped stirrer were provided. The apparatus was kept in an oil-bath at 75° (electrically heated); the bath-temperature gave a most satisfactory temperature gradient for cooling the pre-heated mixtures. Reproducibility of freezing points within 0.002° was readily attained.

Naphthalene (C.P. grade of J. T. Baker Co.) had the freezing-point constant of 7.20, determined with triphenylmethane and *p*-di-*tert*-butylbenzene as reference substances.

Cryoscopic Molecular Weights.—The results obtained are recorded below in groups, according to the compound families.

Monosubstituted phosphonous acids. The acids were obtained conventionally by heating phosphorus trichloride with the aromatic compounds in the presence of aluminum chloride (the dimethylaminophenyl compound did not require the use of the catalyst), followed by treatment of the dichlorophosphines with an excess of warm ethanol, and a final brief boiling with water. This procedure for hydrolysis of dichlorophosphines gives much purer phosphonous acids than are obtained by means of simple aqueous hydrolysis (Kosolapoff, *J. Amer. Chem. Soc.*, 1950, in the press).

The m. p.s of the acids and the solvent from which their final crystallization was carried out are in the table. *p*-Dimethylaminophenylphosphonous acid, m. p. 160—162° (from aqueous alcohol), was too sparingly soluble for cryoscopy.

Molality.	ΔT_f .	Mol. wt.	Molality.	ΔT_f .	Mol. wt.
<i>Phenylphosphonous acid</i> , m. p. 86° (from benzene).			<i>p</i> -Methoxyphenylphosphonous acid, m. p. 116—117° (from benzene).		
0.0684	0.200°	350	0.0567	0.164°	428
0.123	0.335	375	0.112	0.316	439
0.249	0.640	399	0.171	0.466	455
0.360	0.872	413	Trimeric mol. wt. 516.		
0.456	1.110	420	<i>p</i> -Chlorophenylphosphonous acid, m. p. 131—132° (from benzene).		
Trimeric mol. wt. 426.			0.0613	0.162	481
<i>p</i> -Tolylphosphonous acid, m. p. 104—105° (from benzene).			0.121	0.300	511
0.0623	0.178	393	0.178	0.438	516
0.125	0.338	416	Trimeric mol. wt. 529.		
0.188	0.500	421	<i>p</i> -Bromophenylphosphonous acid, m. p. 142° (from benzene).		
Trimeric mol. wt. 468.			0.0456	0.130	559
			0.0889	0.240	589
			0.133	0.345	612
			Trimeric mol. wt. 663.		

Phosphonic acids. The aromatic members were obtained by oxidation of the corresponding phosphonous acids by a warm solution of mercuric chloride. The aliphatic members were prepared conventionally from the alkyl halides and sodium dibutyl phosphite (Kosolapoff, *J. Amer. Chem. Soc.*, 1945, **67**, 1180).

None of the aromatic members was sufficiently soluble in naphthalene to give significant results. The depressions of the freezing point secured with minute samples indicated a very high order of association. The substances used included phenyl- (m. p. 162—163°), *p*-tolyl- (m. p. 189—190°), *p*-methoxyphenyl- (m. p. 166°; apparently a monohydrate), *p*-chlorophenyl- (m. p. 187°), and *p*-bromophenylphosphonic acid (m. p. 193—194°).

Molality.	ΔT_f .	Mol. wt.	Molality.	ΔT_f .	Mol. wt.
<i>n</i> -Butylphosphonic acid, m. p. 106—107° (from light petroleum).			<i>n</i> -Hexylphosphonic acid, m. p. 104—105° (from light petroleum).		
0.0742	0.115°	641	0.0585	0.087°	804
0.149	0.205	724	0.116	0.157	882
0.265	0.330	796	0.169	0.214	942
0.368	0.430	850	Hexamer mol. wt. 997.		
0.455	0.510	906			
0.554	0.583	945			
0.681	0.670	1010			
Hexamer mol. wt. 829.					

Disubstituted phosphonous acids. These substances were prepared either by means of the modified Friedel-Crafts reaction (Kosolapoff and Huber, *J. Amer. Chem. Soc.*, 1947, **69**, 2020) or by the modified Grignard synthesis (Kosolapoff, *ibid.*, 1949, **71**, 369). The aliphatic compounds, obviously, were obtainable only by the latter method.

Neither the di-*o*-methoxyphenyl nor the bis-*p*-dimethylaminophenyl derivative was sufficiently soluble to give significant results; the m. p.s were 227—228° and 211°, respectively.

Molality.	ΔT_f .	Mol. wt.	Molality.	ΔT_f .	Mol. wt.
<i>Di-n-butylphosphonous acid</i> , m. p. 70—71° (from water).			<i>Di-p-tolylphosphonous acid</i> , m. p. 135—136° (from dilute ethanol).		
0.0643	0.223°	370	0.0412	0.148°	494
0.117	0.396	380	0.0726	0.252	511
0.164	0.546	386	0.0988	0.343	510.5
Dimeric mol. wt. 356.			Dimeric mol. wt. 492.5.		
<i>Di-n-hexylphosphonous acid</i> , m. p. 78—79° (from dilute ethanol).			<i>Di-p-chlorophenylphosphonous acid</i> , m. p. 137—138° (from dilute ethanol).		
0.0478	0.160	507	0.0349	0.110	655
0.0876	0.295	501	0.0652	0.195	691
0.129	0.436	498	0.0984	0.285	714
Dimeric mol. wt. 469.			Dimeric mol. wt. 574.		
<i>Diphenylphosphonous acid</i> , m. p. 190—192° (from dilute ethanol).			<i>Di-p-methoxyphenylphosphonous acid</i> , m. p. 179—180° (from dilute ethanol).		
0.0453	0.140	508	0.0369	0.127	582
0.0893	0.270	520	0.0742	0.248	585
Dimeric mol. wt. 436.			Dimeric mol. wt. 556.		

The solubility of this acid was very limited.

Phosphinous acid. The sole example, bis-*p*-dimethylaminophenylphosphinous acid, was prepared essentially according to Raudnitz (*Ber.*, 1927, **60**, 743) and had m. p. 165—166° (from benzene).

Molality.	ΔT_f .	Mol. wt.	Molality.	ΔT_f .	Mol. wt.
0.0347	0.244°	295	0.0689	0.468°	305
Monomeric mol. wt. 288.					

Diethyl phosphite. This substance gave reproducible values of 138—141 for its molecular weight in the range of 0.05—0.13 molality. Since its monomeric molecular weight is 138, no significant deviation from monomer structure was detectable.

Di-n-butyl phosphite. This substance similarly showed no significant deviation from the monomeric state (mol. wt. 194).

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