Phosphinic and Phosphonic Acids I:  
Protonation and Complex Formation Equilibria of Some Substituted  
Ethane-1,1,2-tris-(P-methyl-phosphinic Acids)

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Phosphinic Acids, Protonation Constants, Complex Formation Constants,  
Alkali Earth Metals, Earth Metals

Protonation constants were determined pH-metrically for 3 selected phosphinic acids of the  
type CHRP*−CHP*₂ (R = phenyl, methyl, t-butyl; P* = CH₃P(O)OH). Complex formation  
equilibria were studied for metal ions Mg(II), Ca(II), Sr(II), Ba(II), Cu(II), Zn(II), Al(III) and  
Ga(III). Particular strong complex formation was observed for Ga(III).

Introduction

Oligophosphonic and -phosphinic acids roused  
significant interest as complexing agents and gained importance in many fields of practical  
chemistry. Particular attention was drawn towards molecules having two or more phosphonic or  
phosphinic acid substituents in vicinal and/or preferably geminal positions attached to the  
ethane fragment. Novel synthetic procedures [1–4] led to structures related to a generalized formula:

\[
\begin{align*}
R \quad P^* & \quad P^* = P(O)(OH) \quad \text{Phosphonic acids} \\
H—C — C— H & \quad R = \text{Me, Et, tBu, Ph} \\
p^* & \quad R = \text{H, Me, tBu, Ph, Mes} \\
p^* & \quad R^* \quad \text{Phosphinic acids}
\end{align*}
\]

While the phosphonic acids represent 6-basic  
acids of the general type H₆L, the 3-basic phosphinic acids will be abbreviated H₃L. We titrated  
those compounds vs. bases and found, that ³¹P{'H}-NMR spectra of the resulting solutions depend significantly on the state of the titration  
equilibrium (the composition of species) and the nature of the base cations. By stopped-flow NMR  
techniques, developed in our laboratories [5, 6], complex dynamic situations involving AB₂, ABC  
and ABX spectral types were observed. A full understanding of these phenomena primarily requires the knowledge of accurate dissociation

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(protonation) and metal complex formation constants. At the stage of our research we combined the analytical, preparative and NMR aspects by joining the expertise available in Szeged and Düsseldorf.

Here we wish to start a series of systematic investigations and report on three selected phosphinic acids:

\[
R \quad P^i & \quad P^j \quad P^k = CH₃P(O)OH \\
H—C — C— H & \quad R = \text{Ph, Me, tBu} \\
p^i & \quad p^j & \quad p^k \quad \text{compounds 1, 2, 3}
\]

The molecules of these compounds contain three specific phosphinic acid groups CH₃P(O)OH. The first one is situated at the chiral C₁ atom, while the non-equivalent geminal pair of phosphinic groups is attached to the C₂ atom. As a result, dissociation and complexation of these compounds are non-trivial processes, in principle involving the more complicated concepts of microscopic stability constants in alternative ligand structures. In aqueous solutions of phenyl and methyl derivatives 1 and 2, the dissociation species H₃₋L⁻ (i = 0–3) exist in a rapid conformational equilibrium or, less probably, in a singular conformer. This situation does not hold for the sterically hindered t-butyl compound 3: while in corresponding species H₃₋L⁻ with i = 0–2, a singular species is detected, for the tri-negative anion two individual rotamers were observed by NMR means [2–4, 6]. In addition, we do expect interactions between the molecular conformations of
our model systems and the donor properties of the corresponding anionic species. E.g., when metal complexes form, there are several possibilities to set up 6- or 7-membered chelate rings.

The aim of our experiments was to study the protonation and metal complex formation equilibria of phosphinic acids 1–3. The classical, macroscopic concept of equilibria will be adopted as a first order approximation to describe the experimental results. A selection of phenyl- and methyl-substituted phosphinic acids 1 and 2 was employed to compare aromatic and aliphatic substituent effects. By comparing the methyl and t-butyl derivatives, 2 and 3, we intended to obtain information about sterical effects induced by these substituents R attached to the ethane skeleton.

The Treatment of Equilibria

The cumulative (overall) formation constant, \( \beta_{qpr} \), of a species is defined on the basis of the following equilibrium (where charges on individual species are omitted for simplicity):

\[
qM + pL + rH^+ \rightleftharpoons M_{qLpH}^r \tag{1}
\]

\[
\beta_{qpr} = \left[ M_{qLpH}^r \right] - \left[ M \right]^{q} - \left[ L \right]^{p} - \left[ H^+ \right]^{r} \tag{2}
\]

If there is no metal complex formation, \( q = 0 \), then only the protonation of the ligand occurs. With \( p = 1 \), species with the composition \( H_1L \) are formed.

\[
rH^+ + L \rightleftharpoons H_1L \tag{3}
\]

\[
\beta_1 = \left[ H_1L \right] \cdot [H^+]^{-1} \cdot [L]^{-1} \tag{4}
\]

The stepwise formation (or protonation) constant, \( K_{n} \), is defined by the following equations:

\[
H^+ + H_{r-1}L \rightleftharpoons H_rL \tag{5}
\]

\[
K_r = \left[ H_rL \right] \cdot [H^+]^{-1} \cdot [H_{r-1}L]^{-1} \tag{6}
\]

The \( K_r \)'s and \( \beta_r \)'s are related by:

\[
\log K_r = \log \beta_r - \log \beta_{r-1} \quad (r = 2 \cdots n) \tag{7}
\]

\[
K_1 = \beta_1 \tag{8}
\]

In subsequent papers, dealing with NMR aspects of compounds 1–3, we will use the conventional dissociation constants, \( K_{sr} \)'s, which are the inverse values to the \( K_r \)'s.

The Principles of Calculations

In the equilibrium systems discussed here, the following reactants can be present: strong acid, e.g. \( \text{HClO}_4 \), \( (T_{OH}) \), strong base e.g. \( \text{NaOH} \) as the titrant, \( (T_{OH}) \), ligand \( (T_L) \), and metal ions \( (T_M) \), where the total concentrations are given in parentheses.

In each point of the titration, the total concentrations can be expressed by the following equations:

\[
T_M = \left[ M \right] + \sum q_j \cdot c_j \tag{9}
\]

\[
T_L = \left[ L \right] + \sum p_j \cdot c_j \tag{10}
\]

\[
T_{OH} - T_{OH} = \left[ H^+ \right] + j r_j \cdot c_j - K_w \cdot [H^+]^{-1} \tag{11}
\]

where \( c_j \) is given by the expression:

\[
c_j = \left[ M_{qLpH}^r \right] = \beta_j \cdot [M]^{q} \cdot [L]^{p} \cdot [H^+]^{-r} \tag{12}
\]

For assumed values of \( q_j, p_j \) and \( r_j \) and \( \beta_r \) (defined by the complex model under consideration), equations (9), (10) and (11) may be solved explicitly on the basis of experimental data. In consequence, the concentrations of individual species present in the equilibrium system and the calculated intensity data (e.g. \( E \) (mV)) are obtained. By comparison of the measured and calculated intensities, correction values are evaluated for the parameters to be refined (here \( \beta_r \)), and the procedure is repeated with the corrected parameters. This procedure is done efficiently by an advanced version of the computer program PH-POT, which was developed by F. G. in the Szeged laboratories [7].

In figures to be shown below, we will use an auxiliary function, \( Z_{H} \), which is indicative for the effective number of protons bound by the protonating species. This variable \( Z_{H} \) is defined by:

\[
Z_{H} = \left( T_{OH} - T_{OH} \right) + K_w \cdot [H^+]^{-1} - [H^+] \cdot T_L^{-1} \tag{13}
\]

Experimental Part

Materials: The phosphinic acid derivatives used were prepared according to [1–4]. All other chemicals were commercial products of analytical grade.

The pH-metric measurements were performed in sodium perchlorate solution of 0.5 mol dm\(^{-3}\) ionic strength at temperatures of 25 (+/−0.1) °C by using an Orion digital potentiometer with an accuracy of 0.1 mV. The measuring electrode was a Beckman glass electrode, and the reference electrode was a RADELKIS OP 820 Ag/AgCl electrode. In the electrode the separating electrolyte solution was 0.5 mol dm\(^{-3}\) sodium perchlorate. During the experiments 50.0 cm\(^3\) of about 5 mM solutions of the \( H_1L \) compounds 1–3 were titrated (under nitrogen atmosphere) with 0.1 mol dm\(^{-3}\) sodium hydroxide also containing 0.4 mol dm\(^{-3}\) sodium perchlorate.
The experimental data were evaluated by an advanced version [7] of the least-squares computer program described earlier. The refinements were carried out for the sum of the squares of the residuals of the electromotive forces \( \sum (J E^2) \). The iterative fit is characterized by standard deviations, \( \sigma \) (mV), of the electromotive forces which are given in the tables by the expression: \( \sigma = \sqrt{\sum (J E^2) / \text{(NMP-NP-1)}} \). NMP denotes the numbers of measured points, while NP stands for the number of parameters to be refined.

The electromotive forces (E) can be described by the extended NERNST equation:

\[
E = E^o + g \cdot \log[H^+] - j_{H^+} \cdot [H^+] - j_{OH^+} \cdot K_w \cdot [H^+]^{-1}
\]

The parameters \( E^o \), \( g \) (59.16 mV at 25 °C), \( j_{H^+} \) and \( j_{OH^+} \) (correction factors for the diffusion potential in the acidic and the alkaline region), and \( K_w \) were determined from blank acid-base titrations [9]. Optimization of only the \( E^o \) values was considered necessary. Parallel measurements were evaluated simultaneously by using the individual data for \( E^o \).

**Results**

As a typical example, the pH-metric titration curve of the phenyl substituted compound 1 and its average number of protons (\( Z_{H^+} \)) vs. base equivalents (\( a \)) curve, are plotted in Fig. 1.

It can be seen that the uptake of 2 protons occurs in the titration range. The protonation constants and their errors (expressed in hundredths) are listed in Table I.
Table I. Protonation and dissociation constants of compounds 1-3, 1-substituted ethane-1,2,2-tris-(P-methyl-phosphinic acids).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>log β of</th>
<th>log K₂</th>
<th>σ [mV]</th>
<th>NMP</th>
<th>pKₙ₁</th>
<th>pKₙ₂</th>
<th>pKₙ₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Phenyl</td>
<td>Phenyl</td>
<td>6.79, 9.19</td>
<td>2.40</td>
<td>1.61</td>
<td>47</td>
<td>1-1.2</td>
<td>2.40</td>
<td>6.79</td>
</tr>
<tr>
<td>2 Methyl</td>
<td>6.41, 8.89</td>
<td>2.48</td>
<td>2.08</td>
<td>96</td>
<td>1-1.2</td>
<td>2.48</td>
<td>6.41</td>
<td></td>
</tr>
<tr>
<td>3 t-Butyl</td>
<td>7.87, 11.49</td>
<td>3.62</td>
<td>2.06</td>
<td>95</td>
<td>1-1.2</td>
<td>3.62</td>
<td>7.87</td>
<td></td>
</tr>
</tbody>
</table>

Obtained from measurements in the presence of metal ions, the pH-metric titration curves of the phenyl derivative 1 are shown in Fig. 1b.

Discussion of Results

Protonation constants: Each of the compounds 1-3 represents a 3-basic acid and consequently is characterized by 3 individual protonation constants. But in our experiments only 2 protonation constants were obtained by simulation of the titration curves. With respect to steric effects it is interesting to note that the first protonation constant of 3, the t-butyl derivative, is significantly larger than those of the methyl, 2, or phenyl, 1, compounds. This fact, together with the larger log K₂, indicates the unexpected high basicity of 3.

Metal complexes: In the case of the phenyl derivative, 1, we tried to determine the stability constants of four alkaline earth metal complexes. We found, however, that the strontium and barium ions form very weak complexes only, and the values of the stability constants obtained are rather uncertain. For the other two derivatives, 2 and 3, therefore, we disregarded the examination of the complexes of Sr(II) and Ba(II) ions. The Ga(III) ion, on the other hand, forms very strong complexes, therefore pH-metric measurements are not needed.

Table II. The composition of the metal complexes and corresponding log β values derived for compound 1: 1-phenylethane-1,2,2-tris-(P-methyl-phosphinic acid).

<table>
<thead>
<tr>
<th>M/H⁺</th>
<th>pH range</th>
<th>T₀/T₉</th>
<th>log β of</th>
<th>MLH</th>
<th>MLH₂</th>
<th>MLH⁻</th>
<th>MH⁻⁴</th>
<th>log K⁰₁⁺MLH</th>
<th>log K⁰₂⁺MLHₒ</th>
<th>σ [mV]</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg²⁺</td>
<td>2.2-11.1</td>
<td>1</td>
<td>4.06</td>
<td>8.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.46</td>
<td>-</td>
<td>4.04</td>
<td>47</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>2.2-11.2</td>
<td>1</td>
<td>3.13</td>
<td>8.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.73</td>
<td>-</td>
<td>1.76</td>
<td>46</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>2.2-11.3</td>
<td>1</td>
<td>*1.35</td>
<td>9.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.20</td>
<td>-</td>
<td>1.83</td>
<td>49</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>2.2-11.2</td>
<td>1</td>
<td>-</td>
<td>*7.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.46</td>
<td>-</td>
<td>2.07</td>
<td>31</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>2.1-7.2</td>
<td>1</td>
<td>6.54</td>
<td>10.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.46</td>
<td>-</td>
<td>1.92</td>
<td>40</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>2.2-8.0</td>
<td>1</td>
<td>5.34</td>
<td>9.06</td>
<td>10.75</td>
<td>-3.17</td>
<td>-</td>
<td>3.72</td>
<td>1.69</td>
<td>3.88</td>
<td>48</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>2.0-9.0</td>
<td>2</td>
<td>8.60</td>
<td>12.05</td>
<td>-0.87</td>
<td>29.46</td>
<td>-</td>
<td>3.45</td>
<td>-</td>
<td>3.88</td>
<td>48</td>
</tr>
</tbody>
</table>
Table III. The composition of the metal complexes and corresponding log$\beta$ values derived for compound 2: 1-methylethane-1,2,2-tris-(P-methyl-phosphinic acid), propane-2,3,3-tris-(P-methyl-phosphonic acid).

<table>
<thead>
<tr>
<th>M</th>
<th>pH range</th>
<th>$T_l/T_m$</th>
<th>log$\beta$ of ML</th>
<th>MLH</th>
<th>MLH$_{-1}$</th>
<th>MH$_{-4}$</th>
<th>log$K_{ML}^{MLH}$</th>
<th>$\sigma$ [mV]</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>2.2–11.2</td>
<td>1</td>
<td>3.67$^{116}_6$</td>
<td>8.28$^{23}_3$</td>
<td>–</td>
<td>–</td>
<td>4.61</td>
<td>1.43</td>
<td>49</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2.2–11.2</td>
<td>1</td>
<td>2.64$^{15}_1$</td>
<td>7.99$^{47}_7$</td>
<td>–</td>
<td>–</td>
<td>5.35</td>
<td>2.28</td>
<td>48</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2.1–7.7</td>
<td>1</td>
<td>5.99$^{28}_1$</td>
<td>9.48$^{47}_5$</td>
<td>1.81$^{38}_3$</td>
<td>–</td>
<td>3.49</td>
<td>3.35</td>
<td>42</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.2–8.9</td>
<td>1</td>
<td>4.71$^{16}_1$</td>
<td>8.27$^{23}_7$</td>
<td>3.44$^{26}_4$</td>
<td>–</td>
<td>3.56</td>
<td>4.61</td>
<td>44</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>2.0–8.4</td>
<td>1</td>
<td>8.10$^{16}_6$</td>
<td>11.08$^{12}_3$</td>
<td>0.23$^{12}_1$</td>
<td>–9.77$^{31}_3$</td>
<td>2.98</td>
<td>3.05</td>
<td>44</td>
</tr>
<tr>
<td>Ga$^{3+}$</td>
<td>1.8–3.5</td>
<td>1</td>
<td>17.71$^{15}_5$</td>
<td>–</td>
<td>–</td>
<td>13.66$^{15}_7$</td>
<td>–</td>
<td>2.94</td>
<td>41</td>
</tr>
</tbody>
</table>

Table IV. The composition of the metal complexes and corresponding log$\beta$ values derived for compound 3: 1-t-butyl-1,2,2-tris-(P-methyl-phosphinic acid), 2,2-dimethyl-butane-3,4,4-tris-(P-methyl-phosphonic acid).

<table>
<thead>
<tr>
<th>M</th>
<th>pH range</th>
<th>$T_l/T_m$</th>
<th>log$\beta$ of ML</th>
<th>MLH</th>
<th>MLH$_{-1}$</th>
<th>MH$_{-4}$</th>
<th>log$K_{ML}^{MLH}$</th>
<th>$\sigma$ [mV]</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>2.2–11.2</td>
<td>1</td>
<td>7.11$^{18}_8$</td>
<td>11.58$^{10}_4$</td>
<td>–</td>
<td>–</td>
<td>4.47</td>
<td>2.08</td>
<td>50</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2.3–11.2</td>
<td>1</td>
<td>5.46$^{8}_8$</td>
<td>10.43$^{14}_4$</td>
<td>–</td>
<td>–</td>
<td>4.97</td>
<td>3.25</td>
<td>48</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2.1–9.5</td>
<td>1</td>
<td>9.93$^{27}_8$</td>
<td>13.56$^{47}_7$</td>
<td>0.84$^{36}_2$</td>
<td>–</td>
<td>3.63</td>
<td>3.84</td>
<td>47</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.1–9.7</td>
<td>1</td>
<td>8.64$^{35}_3$</td>
<td>12.53$^{38}_8$</td>
<td>0.67$^{37}_5$</td>
<td>–</td>
<td>3.89</td>
<td>4.53</td>
<td>46</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>2.1–10.8</td>
<td>2</td>
<td>9.84$^{13}_8$</td>
<td>12.39$^{16}_3$</td>
<td>1.09$^{17}_3$</td>
<td>–36.57$^{73}_2$</td>
<td>2.55</td>
<td>2.36</td>
<td>49</td>
</tr>
<tr>
<td>Ga$^{3+}$</td>
<td>1.9–5.4</td>
<td>1</td>
<td>&gt;27.2$^{75}_7$</td>
<td>–</td>
<td>&gt;23.4$^{77}_7$</td>
<td>–</td>
<td>–</td>
<td>2.72</td>
<td>41</td>
</tr>
</tbody>
</table>

The existence of two magnesium and calcium complexes could be substantiated, which corresponds to our expectations. It can be seen in Tables II, III and IV, that the stability of the ML complexes of the copper(II) and zinc ions is considerably higher than that of the two alkaline earth metal complexes. Regarding the MHL complexes, it can be stated that their stability is the lower the higher the stability of the ML species. This tendency suggests that the formation of ML complexes results in a strong electron transfer from the ligands to the metal ions, which decreases the basicity of the uncoordinated donor oxygens. This tendency seems to be confirmed for aluminium, too, which forms the most stable complexes. However, it is surprising that there is not a great difference between the protonation constants of the ML complexes with the different ligands; their values are about 4.5, 5.2, 3.5 and 3.7 for magnesium, calcium, copper(II) and zinc, respectively.

Conclusions

Within the range of pH-measurements as presented here, (2.2–11), the compounds 1–3 take up only 2 protons. All our efforts to calculate the third protonation constant failed.

Our calculations show, however, that the missing pK$_1$ cannot be greater than 1.0–1.2. Particular attention is drawn to a comparison of the methyl and t-butyl derivatives 2 and 3. Although one can expect a higher basicity for the t-butyl compound, the value found surpasses our expectations. Of the metal ions examined, the alkaline earth metals form relatively weak complexes. Examination of the stability constants clearly shows that their complex-forming tendency decreases with a corresponding increase of cationic radii. The copper(II), zinc and aluminium complexes conform to this conclusion. For the Cu(II), Al(III) and Zn(II) ions, which are easily hydrolyzed, formation of the monohydroxo complex does occur. The stability is
not very high, however, and both the copper(II) and zinc complexes irreversibly decompose up to about pH 9.6. It is not substantiated by our measurements, but it can be assumed that the formation of 6- or 7-membered chelate rings can play a role in the stability of the hydroxo complexes. The evaluation of the measurements available does not indicate the presence of other, e.g. binuclear or bis-complexes.

In subsequent publications we will report on NMR studies of protonation and complex formation equilibria.

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