Investigation on the Extraction of Metal Ions with Different Organophosphorus Compounds. I. The Dissociation, Distribution and Dimerization of Some Di-aryl Esters of Orthophosphoric Acid

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The net distribution ratio \( q \) of several di-aryl esters of orthophosphoric acid between chloroform and \( 1 \text{M} \) (or \( 0.1 \text{M} \)) \( \text{HClO}_4 - \text{NaClO}_4 \) solutions has been studied. The distribution of the acids has been measured spectrophotometrically, except in the case of di-(benzyl) phosphate, where a radiometric method has been applied using acid labelled with \( ^{32} \text{P} \). Varying the composition of the aqueous and the organic phase a number of data were obtained from which, by fitting the normalized curve \( \log y = \log (x+1) \), the dissociation, distribution and dimerization constants of the investigated acids were calculated. The values of these constants are given in Table II.

Following the equation given by Hammett, the strength as well as the association of the investigated acids can be satisfactorily explained assuming that the inductive polar effect of the substituents affects their dissociation and dimerization constants. The results allow to predict the values of these constants for the orthophosphoric acids carrying other substituents.

INTRODUCTION

It is well known that, for an elaborate treatment of the extraction data it is necessary to know the values of the dissociation, distribution and dimerization constants of the acid form of the reagents which form extractable complexes with the metal ions. The values of those constants affect the concentration of the various reagent species in a given extraction system and allow one establish extraction mechanism and composition of the complexes formed. Of the different esters of phosphoric acid at present largely used as extracting agents for the metal ions, so far only the di-alkyl phosphates and especially the di-\( n \)-butyl phosphate have been investigated\(^{1,2,11}\). However, only very limited work has been done concerning the physicochemical properties and the extraction abilities of di-aryl orthophosphates. Recently Peppard et al.\(^3\) reported some physical properties, such as molecular weight, density, refraction index, viscosity and infrared spectra of several di-aryl esters of orthophosphoric acid.

It was the aim of the present investigation to show how the introduction of an aromatic substituent affects the dissociation, distribution and dimerization constants of the resulting aromatic orthophosphate and to establish the influence of the structure change on the physico-chemical properties of the resulting compounds.
Preparation of the reagents: Several di-arylphosphates \((\text{RO})_2\text{POOH}\), where \(R\) is phenyl, \(p\)-tolyl, \(p\)-chlorophenyl, benzyl and \(\beta\)-naphthyl, were prepared following the method given by Welcher\(^4\), based upon the reaction between \(\text{POCl}_3\) and the respective alcohol. The resulting reaction mixture contains the corresponding mono- and dichloride derivates, which were separated by distillation in vacuo. The monochlorides were hydrolized by aqueous NaOH solution and the obtained orthophosphates further purified by recrystallization from a suitable organic solvent or from water.

The elemental analyses for carbon, hydrogen and phosphorus, as well as melting points, are listed in Table I. The results obtained showed the compounds to be sufficiently pure for further investigations.

<table>
<thead>
<tr>
<th>Orthophosphoric Acid</th>
<th>Symbol</th>
<th>C</th>
<th>H</th>
<th>P</th>
<th>Melting point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-(phenyl)·2H(_2)O</td>
<td>HDPP</td>
<td>50.30</td>
<td>49.43</td>
<td>5.29</td>
<td>10.82</td>
</tr>
<tr>
<td>Di-(p-tolyl)</td>
<td>HDTP</td>
<td>60.30</td>
<td>59.84</td>
<td>5.44</td>
<td>11.13</td>
</tr>
<tr>
<td>Di-(p-chlorophenyl)</td>
<td>HD-pCl-PP</td>
<td>45.18</td>
<td>44.50</td>
<td>2.84</td>
<td>9.71</td>
</tr>
<tr>
<td>Di-(benzyl)</td>
<td>HDBzP</td>
<td>60.30</td>
<td>59.91</td>
<td>5.44</td>
<td>11.13</td>
</tr>
<tr>
<td>Di-((\beta)-naphtyl)</td>
<td>HDNP</td>
<td>68.57</td>
<td>68.10</td>
<td>4.32</td>
<td>8.84</td>
</tr>
</tbody>
</table>

Characterization of reagents: To determine dissociation constants \((K_a)\), the distribution constants of the monomeric form \(HA\) between the organic and the aqueous phase \((K_d)\), as well as the dimerization constant in the organic phase \((K_2)\) of the acids investigated, the method used previously by Dyrssen\(^1\) in the case of di-\(n\)-butyl phosphate (HDBP) has been applied. This method is based on the measurement of the net distribution ratio \(q\) of the acids under different experimental conditions. For this purpose solutions of \((\text{RO})_2\text{POOH}\) in chloroform were shaken for 1 hour with an equal volume of the aqueous phase containing a 1 M solution of \(\text{HClO}_4\) and \(\text{NaClO}_4\), so that the ionic strength of the aqueous phase was kept constant in all of the experiments. The equilibration of both phases was carried out in 50 ml stoppered centrifuge tubes at ambient temperature, which was kept approximately constant \((20±2°C)\). As organic phase chloroform, previously washed with water to remove alcohol acting as stabilizer, was used. After equilibration the phases were separated by centrifugation. The distribution ratio was measured spectrophotometrically using a spectral photometer CF4 Optica Milano. The light absorption curves of the chloroform solutions of \((\text{RO})_2\text{POOH}\) exhibit a sharp peak in the spectral range from 258 to 276 m\(\mu\). Since extinction in the aqueous phase depends to some extent upon the concentration of hydrogen ions as well as upon its ionic strength, the concentration of acids in the organic phase after equilibration was always measured \((c_{\text{org}})\). Knowing this concentration the net distribution ratio \(q\) could be calculated as

\[
q = \frac{c_{\text{org}}}{C_{\text{tot}} - c_{\text{org}}}
\]

If the major part of the acids remains in the chloroform phase, an aliquot part of the aqueous phase was separated, acidified with \(\text{HClO}_4\) to obtain 2 M \(\text{HClO}_4\).
and reextracted in fresh chloroform. The concentration of \((RO)_2POOH\) in chloroform after the second extraction represents \(c_{aq}\). In such cases \(q\) was calculated as

\[
q = \frac{c_{tot} - c_{aq}}{c_{aq}}
\]

In the case of HDBzP this reagent labelled with radioactive \(^{32}\)P was prepared and the distribution measured radiometrically in a 10 ml liquid counter (type M6H, 20th Century Electronics). An appropriate correction was introduced to compensate differences in density of both phases.

The hydrogen ions concentration was measured with a Radiometer valve potentiometer equipped with glass and calomel electrodes. The electrodes were standardized against a 0.1 \(M\) \(HClO_4\) — NaClO_4 buffer (pH = 2.00). If the hydrogen ions concentration was higher than 0.1 \(M\), it was calculated from the amount of acid added.

**RESULTS**

a) *Dimerization Constants of \((RO)_2POOH\)*

To determine dimerization constants of our diaryl phosphates, their chloroform solutions were shaken with an equal volume of \(10^{-1} M\) \(HClO_4\). In the case of HDNP, HDBzP and HDTBP, \(10^{-2} M\) \(HClO_4\) was used. The concentration of \(HClO_4\) in the latter case is very low and it would be expected that the dissociation of \((RO)_2POOH\) will affect \([H^+]\). However, owing to their high distribution constants, \([HA]\) is always low, so that \([H^+]\) may be taken as constant. Only at higher initial HDTBP concentrations \([H^+]\) markedly deviates from \(10^{-2} M\) but at lower HDTBP concentrations this deviation disappears. The initial concentration of the acids in chloroform varied in the following ranges: \(10^{-1}\) to \(10^{-4}\) \(M\) for HDpCl-PP, \(10^{-1}\) to \(5.10^{-4}\) \(M\) for HDPP, \(3.10^{-2}\) to \(2.10^{-4}\) for HDTBP, \(1.10^{-2}\) to \(1.10^{-4}\) for HDNP and HDBzP. After equilibration and separation of both phases the distribution of the acids was measured. If we assume that the undissociated monometric form \(HA\) and the anion \(A^-\) are the species of \((RO)_2POOH\) in the aqueous phase

\[
c_{aq} = [HA] + [A^-]
\]

whereas the dimer \(H_2A_2\) and the monomer \(HA\) are the species in chloroform

\[
c_{org} = 2[H_2A_2]_{org} + [HA]_{org}
\]

and of we use the definitions of \(K_a\), \(K_d\) and \(K_2\)

\[
K_a = [H^+][A^-]/[HA]^* \\
K_d = [HA]_{org}/[HA] \\
K_2 = [H_2A_2]_{org}/[HA]^2_{org}
\]

the net distribution ratio \(q\) can be written as

\[
q = c_{org}/c_{aq} = 2 K_2 (K_d/\varphi)^2 c_{aq} + K_d/\varphi
\]  

where \(\varphi\) represents

\[
\varphi = 1 + K_a/[H^+]
\]

* The correct expression for the dissociation constant \(K_a\) would be:

\[
K_a = (H^+) (A^-) \cdot \gamma_{H^+} \cdot \gamma_{A^-} / (HA) \cdot \gamma_{HA}
\]

where the expression in parantheses denotes concentrations and \(\gamma\)’s are the activity coefficients. As all dissociation reactions are very similar in type and ionic strength was always kept constant, the distinction between the activities and concentrations can be ignored.
Equation (1) can be solved graphically following the curve-fitting method given by Dyrssen and Sillén. If log $q$ is plotted against log $c_{aq}$ the experimental points should follow the normalized curve log $y = \log(x + 1)$ very well. According to eqn. (1) from the horizontal asymptote of the curve ($x = c_{aq} \to 0$) the value of log $K_a/q$ is obtained, whereas the point of intersection of the asymptotes of the curve gives log $2K_a(K_a/q)$.

Fig. 1. Distribution of different diaryl phosphoric acids between chloroform and 0.1 M or 0.01 M HClO$_4$—NaClO$_4$ solutions as a function of the total concentration of the acids in the aqueous phase. The normalized curve log $y = \log(x + 1)$ is fitted to the data.

Fig. 1 represents the plots log $q$ versus log $c_{aq}$ for all investigated acids. The values for their dimerization constants obtained by this method are given in Table II.

**Table II**

The dimerization, dissociation and distribution constants of diaryl phosphoric acids including Taft constants $\sigma^*$ of the corresponding substituents

<table>
<thead>
<tr>
<th>Orthophosphoric acid</th>
<th>log $K_2$</th>
<th>$pK_a$</th>
<th>log $K_a$</th>
<th>log $K_a$</th>
<th>$\sigma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in 0.1 M</td>
<td>in 1 M</td>
<td>from eqn. 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ClO$_4^-$</td>
<td>ClO$_4^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-(p-chlorophenyl)</td>
<td>3.44</td>
<td>0.20</td>
<td>0.80</td>
<td>0.58</td>
<td>0.56</td>
</tr>
<tr>
<td>di-(phenyl)</td>
<td>3.76</td>
<td>0.26</td>
<td>$-0.30$</td>
<td>$-0.50$</td>
<td>$-0.51$</td>
</tr>
<tr>
<td>di-(p-tolyl)</td>
<td>4.24</td>
<td>0.40</td>
<td>0.78</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>di-(benzyl)</td>
<td>3.90</td>
<td>0.70</td>
<td>1.26</td>
<td>—</td>
<td>0.92</td>
</tr>
<tr>
<td>di-(o-naphtyl)</td>
<td>4.62</td>
<td>0.74</td>
<td>1.78</td>
<td>1.62</td>
<td>1.66</td>
</tr>
<tr>
<td>di-(n-butyl)$^b$</td>
<td>4.48</td>
<td>1.00</td>
<td>0.33</td>
<td>0.33</td>
<td>0.34</td>
</tr>
</tbody>
</table>

a) the values taken from the work given by Dyrssen
b) the values taken from Neuman

$^c$ calculated values assuming approximate additive and proportional nature for $\sigma^*$. 
**b) Dissociation and Distribution Constants of \((RO)_2\text{POOH}\)**

In order to determine both the dissociation and the distribution constants of \((RO)_2\text{POOH}\) acids, their partition between the organic and the aqueous phase as a function of acidity in the aqueous phase has been measured. The initial concentration of the acids in the chloroform phase was kept constant, its actual value depends upon the molecular extinction coefficient of the individual acid and was \(4.10^{-3} \text{M}\) for HDPP, \(7.10^{-4} \text{M}\) for HDTP, \(8.10^{-4} \text{M}\) for HD-pCl-PP, \(1.10^{-4} \text{M}\) for HDNP and \(3.7.10^{-4} \text{M}\) for HDBzP. The ionic strength of the aqueous phase was \(0.1 \text{M}\) or \(1 \text{M}\), and this phase contained \(\text{HClO}_4\) and \(\text{NaClO}_4\) in different ratios. As in the precedent set of experiments, the net distribution ratio \(q\) was measured spectrophotometrically, except in the case of HDBzP, where a radiometric method could be applied.

The net distribution ratio in these experiments in defined as

\[
q = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}] + [\text{A}^-]}
\]

and using the definition for \(K_a\) and \(K_d\) we obtain

\[
q = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}] (1 + K_a / [H^+])} = K_d / (1 + K_a / [H^+])
\]

or

\[
K_d/q = K_a / [H^+] + 1
\] (2a)

Again the graphical method can be applied to obtain the values of \(K_a\) and \(K_d\) from eqn. (2). The normalized curve \(\log y = \log (x + 1)\) as in the previous case fits the data if \(\log q\) (-\(\log y\)) is plotted versus \(\log [H^+]\) (-\(\log x\)). In this case the horizontal asymptote \((x = 1/[H^+] \to 0)\) gives \(\log K_a\), and the point of intersection of the two asymptotes gives \(\log K_d\). As it was shown in the preceding part, very strong dimerization of \((RO)_2\text{POOH}\) acids in...
chloroform takes place and therefore the value of q corrected for the formation of dimers in CHCl₃ must be used in the plot. Knowing the dimerization constants of (RO)₂POOH in chloroform, the following formula was developed to calculate such corrected values of q:

\[
[HA]_{\text{org}} = \frac{-1 + \sqrt{1 + 8K_2 C_{\text{tot}}q/(1 + q)}}{4K_2}
\]

and

\[q_{\text{corr}} = (q + 1) \frac{[HA]_{\text{org}}}{C_{\text{tot}}}
\]

where \(C_{\text{tot}}\) is the initial concentration of (RO)₂POOH in chloroform and q is the net distribution ratio obtained experimentally (the phase volumes were equal).

The results from this set of experiments are given graphically in Fig. 2 and 3, where \(\log q_{\text{corr}}\) is plotted against \(\log [H^+]\). The values \(\log K_a\) and \(\log K_d\) for different diaryl phosphates obtained from those experiments are listed in Table II. Within the limits of experimental error, \(pK_a\) in 0.1 M and 1 M NaClO₄ are the same. This was also found for HDBP by Dyrsen.

Using the values for \(\log K_a\) found in this set of experiments, the distribution constants \(K_d\) can be recalculated from the horizontal asymptote \(\log K_d/q\) in the preceding part. Those recalculated values are given in the 6th column of Table II. The agreement between the two values is good.

c) Simultaneous Determination of the Product of all Constants

To check the accuracy of the constants \(K_a\), \(K_1\) and \(K_2\) found in the previous parts, a set of experiments was carried out in order to obtain the product of all constants. For this purpose solutions of (RO)₂POOH of different concen-
trations in chloroform were shaken with an equal volume of 0.1 M NaClO₄ and after the separation of the phases, the acidity was measured in the aqueous phase. This procedure has been used in the concentration range from 10⁻² to 1 M or up to the concentration limited by the solubility of the acids in chloroform.

It was assumed that \( c_{\text{tot}} = c_{\text{org}} + c_{\text{aq}} = 2[H_2A_2]_{\text{org}} + [HA]_{\text{org}} + [HA]^+ + [A^-] \) and, since the aqueous phase was a neutral NaClO₄ solution, \([A^-] = [H^+]\). Those assumptions and the definitions of \( K_a \), \( K_d \) and \( K_2 \) lead to the following expression for \( c_{\text{org}} \):

\[
c_{\text{org}} = 2 K_2 \left( K_d/K_a \right)^2 [H^+]^2 [A^-]^2 + (K_d/K_a) [H^+] [A^-] \tag{3}
\]

\( c_{\text{org}} \) can be calculated using the equation

\[
c_{\text{org}} = c_{\text{tot}} - c_{\text{aq}} = c_{\text{tot}} - [A^-] - [HA] = c_{\text{tot}} - [H^+] - [H^+]^2 / K_a \tag{4}
\]

The results are given in Fig. 4, where \( \log c_{\text{org}} \) is plotted versus \( \log [H^+] [A^-] \). The plots represent straight lines with the slope equal to 2. This means that the last term in eqn. (3) can be neglected, i.e., that in the concentration range investigated only dimers are present in the organic phase. Furthermore, it means that \( H_2A_2 \) in the aqueous phase can be neglected. From the position of the straight lines the values \( \log K_2 \left( K_d/K_a \right)^2 \) can be calculated.

![Fig. 4. Distribution of some diaryl phosphoric acids between chloroform and 0.1 M NaClO₄.](image)

**TABLE III**

Values of \( \log K_2 \left( K_d/K_a \right)^2 \) obtained by two different sets of experiments (see text)

<table>
<thead>
<tr>
<th>Orthophosphoric Acid</th>
<th>( \log K_2 \left( K_d/K_a \right)^2 ) from Table II</th>
<th>( \log K_2 \left( K_d/K_a \right)^2 ) from exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-(p-chlorophenyl)</td>
<td>5.00</td>
<td>3.38</td>
</tr>
<tr>
<td>Di-(phenyl)</td>
<td>3.28</td>
<td>5.06</td>
</tr>
<tr>
<td>Di-(p-tolyl)</td>
<td>6.32</td>
<td>6.32</td>
</tr>
</tbody>
</table>
In Table III these values of \( \log K_a(K_d/K_a)^2 \) are compared with values calculated from Table II. The disagreement is not too serious and probably within the limits of experimental error.

\( K_a \) found in the previous part was used to calculate \( c_0 \) in eqn. (4). As [HA] is always very low in comparison with [A\(^-\)], the error in \( K_a \) would only slightly affect the value of \( \log K_a(K_d/K_a)^2 \) found in this set of experiments.

**DISCUSSION**

The results show that diaryl esters of orthophosphoric acid are much stronger acids than phosphoric acid itself (\( pK_a = 2.12 \)). Dyrrsen suggested that this was due to the fact that orthophosphoric acid is stabilized by internal hydrogen bonds while the hydrogen bonding in its diesters is disturbed by the free rotation of the two ester groups. Comparing our diaryl phosphates with the dialkyl phosphates which were investigated by Kumler and Eiler and by Dyrrsen, it can be observed that the diaryl esters are the stronger acids. This can be satisfactorily explained by considering the effect of a given substituent from the point of view of electrostatics. In the reversible acid dissociation reaction

\[
HA \rightleftharpoons H^+ + A^- 
\]

with the dissociation constant \( K_a \), the standard free-energy change \( \Delta F \) is given by the equation

\[
\Delta F = -RT \ln K_a 
\]

For a second dissociation reaction

\[
\Delta F' = -RT \ln K_a'
\]

and combining both equations it follows that

\[
\Delta \Delta F = \Delta F - \Delta F' = -RT \ln (K_a/K_a')
\]

Thus the substituents affect the value of \( \Delta F \) of the acid dissociation reaction, which can be due to their electrical pole producing a shift of the electrons within the molecule. If by the action of a substituent the electron charge density in the vicinity of an ionizable proton decreases, the \( \Delta F \) value is lowered and hence the dissociation constant increases (\( pK_a \) decreases). Consequently, the substituents producing an electron withdrawing polar effect increase the acid strength, whereas the substituents releasing the electrons have the opposite effect. Groups containing unsaturated carbon-to-carbon linkages (and the phenyl group is such a group) exhibit an electron withdrawing polar effect, while the alkyl groups release the electrons. It is therefore quite reasonable that diaryl orthophosphates are stronger acids than the corresponding dialkyl phosphates.

The most successful quantitative correlation between the structure of a chemical compound and the equilibrium constants of its reactions is the Hammett equation

\[
\log \left( \frac{k}{k_o} \right) = \sigma \rho
\]

where \( k \) and \( k_o \) are corresponding equilibrium constants with and without a given substituent, \( \rho \) is a proportionality constant, dependent upon the nature
of the reaction, and $\sigma$ is a substituent constant representing a quantitative measure of the inductive, resonance or kinetic-energy type polar effects of a given substituent relative to a hydrogen atom.

$$R,O$$

Fig. 5. a) Relationship between $pK_a$ of diaryl phosphoric acids and $\Sigma\sigma^*$ of their substituents. b) Relationship between $\Delta\nu_{\text{OD}}$ and $\Sigma\sigma^*$ of several (RO)$_2$PO and RO compounds. TBP, TZZP and TPP are tributyl-, tribenzyl, and triphenyl phosphate. RO are following aliphatic ethers: 1 = di-iso-propyl-, 2 = diethyl-, 3 = di-n-propyl-, 4 = di-n-butyl-, 5 = dibenzyl-, 6 = dichloroethyl ether respectively. The values for RO are taken from Mave! II.

In our case it would be more convenient to consider only the net inductive polar effect of the substituents, which is expressed by the Taft constant $\sigma^*$. The reason for this is the fact that the phosphorus atom isolates the resonance effect of the substituents. The values of $\sigma^*$ for the substituents incorporated in our diaryl phosphates are represented in the last column of Table II. The values $\sigma^*$ for the p-tolyl and p-chlorophenyl groups were calculated assuming their approximate additive and proportional nature.

In Fig. 5a the values for $pK_a$ of different (RO)$_2$POOH acids are plotted against $\Sigma\sigma^*$ values of the corresponding substituents. It is evident that the points follow a straight line in support of the explanation that the inductive polar effect of the substituent affects the strength of the corresponding acids.

On the basis of our results it could be expected that substituents such as p-fluorophenyl, p-nitrophenyl or p-trichloromethylphenyl, which are still more electronegative than p-chlorophenyl would further increase the strength of the corresponding orthophosphoric acid. This is mentioned because it is assumed that a structural change leading to a lower $pK_a$ for the chelating reagent would improve its extraction abilities.

It was shown by several authors \(^{1-9} \) that the association of (RO)$_2$POOH acids in organic solvents is very strong. The tendency to associate is due to the property of the $\text{P}^{\circ}$ group to form hydrogen bonds. So far only in the case of carboxylic acids (which because of the $-\text{C}^{\circ}$ group also show
a tendency to dimerize) the relationship between the strength of the hydrogen bridge and the acidity and basicity of the proton donor and acceptor moieties has been investigated. In this connection some discrepancies in the correlation between acid strength and tendency to dimerize can be observed. Allen and Caldin\textsuperscript{12} stated that the dimerization of carboxylic acids in benzene increases with decreasing acid strength and the same results were obtained by Barton and Kraus\textsuperscript{13} who investigated several other carboxylic acids. On the other hand, Brown and Mathieson\textsuperscript{14} reported that in a given solvent the more highly chlorinated acetic acids are more highly associated, which is in disagreement with the preceding assumption. Our results, represented in Table II, show that with the exception of di-(p-tolyl) phosphoric acid the order of dimerization constants in chloroform is the same as that of their \( pK_a \) values in water. So it may be concluded that the degree of dimerization as well as the dissociation in water depend upon the magnitude of the inductive polar effect of the substituent. Electron withdrawing substituents decrease the basicity of the phosphoryl oxygen and therefore their tendency to accept the proton is decreased. Simultaneously the acidity of the hydroxyl hydrogen increases. Thus the two effects are opposite.

The change of acidity as a function of the Taft \( \sigma^* \) value of the substituents is expressed by the constant \( \varphi \) in the Hammet-Taft equation. The value \( \varphi \) is given by the slope of the straight line when \( pK_a \) is plotted against \( \Sigma \sigma^* \). The value \( \varphi = 3.9 \) was estimated for aliphatic alcohols\textsuperscript{15} and \( \varphi = 1.72 \) for carboxylic acids\textsuperscript{16}. From Fig. 5a the value \( \varphi = 0.5 \) was obtained for our diaryl phosphoric acids. The very low value in the latter case is partly due to the relatively large distance between the substituents and the ionizable OH group. Some other results\textsuperscript{17} indicate that the inductive effect of the substituents on the ionic bonds is rather small. This would probably be the principal reason for the low susceptibility of the OH bond in diaryl phosphoric acids i.e. for the low value of the constant \( \varphi \) in the Hammet-Taft equation.

In order to illustrate the influence of the substituents on the basicity of the phosphoryl oxygen, the association of three neutral phosphates with deuterated methanol in \( \text{CCl}_4 \) was measured with a Perkin-Elmer infrared spectrophotometer Mod. 21. The initial concentration of the phosphates was 0.5 — 1 M and that of \( \text{CH}_3\text{OD} \) 1.10\textsuperscript{-2} — 5.10\textsuperscript{-3} M. According to Gordy\textsuperscript{18} the frequency shift \( \Delta V_{\text{OD}} \) of the stretching vibration of the free and associated OD group can be taken as a measure of the basicity of the phosphoryl oxygen. The results are given in Fig. 5b, where \( \Delta V_{\text{OD}} \) is plotted against \( \Sigma \sigma^* \). The points lie approximately on a straight line with the slope \( \Delta V_{\text{OD}}/\Sigma \sigma^* \) equal to 20. An investigation of the association between several dialkyl ethers and \( \text{CH}_3\text{OD} \) carried out by Mavel\textsuperscript{19} gives the value \( \Delta V_{\text{OD}}/\Sigma \sigma^* \), approximately equal to the one presently obtained (see Fig. 5b). This indicates that the change of basicity of the phosphoryl and alkyl ethers oxygen as a function of the polarity of the substituents is quite similar. However, the change of acidity of the OH bond as a function of the polarity of the substituents, which is expressed by the Hammet-Taft constant \( \varphi \), is much lower in the case of the corresponding diaryl phosphoric acids than in the case of the corresponding alcohols. This suggests the assumption that the basicity of the phosphoryl
oxygen is the prevalent factor affecting the dimerization of diaryl phosphoric acids in organic solvents.

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15. see Ref. 7, p. 607.
17. D. Hadži and J. Jan, unpublished work.

IZVLEČEK

Preiskava ekstrakcije metalnih ionov z različnimi organofosfornimi spojini. I.
Disociacija, porazdelitev in dimerizacija nekaterih di-arilnih estrov fosforne kisline

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Določali smo porazdelitvene koeficiente nekaterih di-arilnih estrov ortofosforne kisline med kloroformom in 1M HClO₄ raztopinami. Porazdelitev kisline smo merili spektrofotometrično, razen v primeru di-benzil fosfata, kjer smo uporabili s 31P zaznamovano kislinjo in to porazdelitev merili radiometrično. S spreminjanjem sastave vodne in organske faze smo dobili veliko število eksperimentalnih podatkov, iz katerih smo z metodo prilagovanja na normalizirano krivuljo log y = log(x+1) izračunali disociacijsko, porazdelitveno in dimerizacijsko konstanto preiskovanih kislin. Vrednosti teh konstant so podane v Tabeli II.

S pomočjo Hammett-ove enačbe je možno tolmačiti jakost, kakor tudi asociacijo preiskovanih kislin, pri čemer predpostavljamo, da čisti polarni efekt substituent vpliva na vrednost njihovih disociacijskih in dimerizacijskih konstant. Dobljeni rezultati omogočajo predvideti vrednost teh konstant za poljubno substi­tuirane estre ortofosforne kislince.