THE NATURE OF THE CHEMICAL BONDING 
IN ORGANO-PHOSPHORUS COMPOUNDS

R. F. HUDSON

Cyanamid European Research Institute, Cologny-Geneva, Switzerland

INTRODUCTION

The great increase in synthetic organo-phosphorus chemistry within the last two decades has greatly stimulated research into the mechanistic and structural fields. Ten years ago, hardly any mechanistic studies of the fascinating reactions of phosphorus compounds had been reported, but we now have considerable understanding of many of them. Mechanistic interpretations must be based on a detailed knowledge of the bonding in the various types of compound and reaction intermediate, and in the following lecture I will try to give a brief account of some of the more important structural features of organo-phosphorus compounds. My main theme will be the strong contrast between nitrogen and phosphorus, and the way in which the electronic structure of phosphorus (Figure 1) determines the molecular structure of the known compounds.

![Diagram showing atomic energy levels for nitrogen, phosphorus, and chromium.]

*Figure 1.* Atomic energy levels for nitrogen, phosphorus and chromium

The electronic structures of phosphorus, nitrogen and chromium, a typical transition element, are compared in Figure 1. In the case of nitrogen, and first row elements in general, 2s and 2p electrons only are used, and the higher 3d orbitals can be neglected. The theoretical interpretation of nitrogen and carbon chemistry is thereby simplified, since these elements exhibit only one valency, and much of organic chemistry is concerned with π-electron systems which are mathematically tractable.

The 3d and 4s electrons in transition elements are of comparable energy,
hence \( d \) orbital bonding makes a major contribution to the energies of their complexes. These elements have low electronegativities, and exist mainly as cations at the centre of planar \( spd^2 \) or octahedral \( sp^3d^2 \) complexes, a situation which is suitable for the application of ligand field theory to electrostatic models.

Second row elements are more difficult to treat theoretically, as the \( 3s-3d \) promotional energy is high, although it is significantly less than that for first row elements. However the mixing of a small amount of a high energy state frequently increases bond energies significantly. Thus Pauling and Simonetta\(^1\) attribute the stability of the tetrahedral structure of \( P_4 \), with angles of 60° to \( spd \) hybridization (with \( \sim 2 \) per cent \( d \) character) giving \( \sim 10 \) kcal/mole of stabilization energy which offsets ring strain. Phosphorus seems to accommodate small angles fairly easily, and this is important in some of its reactions and re-arrangements.

**COMPARISON OF NITROGEN AND PHOSPHORUS**

There are two main and important differences between nitrogen and phosphorus, namely the difference in \( p_\pi-p_\pi \) bonding and in \( d \)-orbital bonding. Phosphorus forms no stable compounds with \( p_\pi-p_\pi \) bonds, whereas the corresponding compounds of nitrogen are very stable. The difference is shown graphically in Figure 2 where the bond orders and bond energies for the two

![Figure 2](image)

*Figure 2. Comparison of the single and multiple bond energies of nitrogen and phosphorus elements are compared, and in Table 1 which gives values of \( \sigma \)- and \( \pi \)-bond energies for several compounds.*

Mulliken\(^2\) has pointed out that \( 3p_\pi-3p_\pi \) overlap integrals are quite large, but that \( 3p_\sigma-3p_\sigma \) bonds are usually stronger than \( 2p_\sigma-2p_\sigma \) bonds, as indicated by the corresponding overlap integrals in Figure 3. Secondly \( P-X \) bonds are more polar than \( N-X \) bonds\(^\dagger\), so that Coulomb forces further strengthen the bonds to phosphorus. This is shown by the data of Table 1, and a similar situation is observed with oxygen and sulphur, and with fluorine and chlorine.

\(^\dagger\) When \( X \) is an electronegative group.
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

Table 1. A comparison of bond lengths and bond energies of diatomic compounds of phosphorus and nitrogen

<table>
<thead>
<tr>
<th>Bond</th>
<th>DAB (kcal/mole)</th>
<th>( r_{AB} ) (Å)</th>
<th>Molecule</th>
<th>DAB (kcal/mole)</th>
<th>( r_{AB} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P—P</td>
<td>50</td>
<td>2.18</td>
<td>( \text{P}_2 )</td>
<td>116</td>
<td>1.894</td>
</tr>
<tr>
<td>P—N</td>
<td>70</td>
<td>1.80</td>
<td>( \text{PN} )</td>
<td>164</td>
<td>1.491</td>
</tr>
<tr>
<td>P—O</td>
<td>86</td>
<td>1.76</td>
<td>( \text{PO} )</td>
<td>143</td>
<td>1.448</td>
</tr>
<tr>
<td>P—S</td>
<td>55</td>
<td>2.14</td>
<td>( \text{PS} )</td>
<td>—</td>
<td>1.92</td>
</tr>
<tr>
<td>P—C</td>
<td>65</td>
<td>—</td>
<td>( \text{PC} )</td>
<td>159</td>
<td>1.562</td>
</tr>
<tr>
<td>N—N</td>
<td>~35</td>
<td>1.40</td>
<td>( \text{N}_2 )</td>
<td>225</td>
<td>1.095</td>
</tr>
<tr>
<td>N—O</td>
<td>48</td>
<td>1.36</td>
<td>( \text{NO} )</td>
<td>162</td>
<td>1.15</td>
</tr>
</tbody>
</table>

† Single bond energies.

Figure 3. Overlap integrals\(^a\) for \( p_{\sigma}—p_{\sigma} \) and \( p_{\pi}—p_{\pi} \) bonds of representative first and second row elements as a function of reduced internuclear distance \( r \)

These differences in bond energies are reflected strongly in the chemistry of trivalent phosphorus and nitrogen.

Thus phosphorus does not form compounds of the type† \( \text{R—P=P=R, R—P=NR, R—P=CR}_2, \text{R—P=O} \), whereas these are the most stable nitrogen compounds. Moreover there is no aromatic phosphorus chemistry corresponding to nitrogen heterocyclic chemistry. In particular we may note that the oxacyclics and their derivatives of nitrogen and phosphorus are completely different as shown by the following examples,

† The \( \pi \)-bond energies given in Table 1, and the observations in the following section suggest that it should be possible to prepare conjugated compounds of these types.

373
PARTICIPATION OF $p_{\pi}-p_{\pi}$ BONDING IN EXCITED STATES

Since many $p_{\pi}-p_{\pi}$ bonded compounds of sulphur are quite stable, and the $p_{\pi}-p_{\pi}$ bond energies for phosphorus compounds given in Table 1 are quite large, this bonding certainly participates in excited states and hence may affect the physical and chemical properties, in particular spectra and reactivity.

(i) The u.v. spectra of phosphines\(^3\) show strong $n-\pi^*$ transitions corresponding to the following electronic change and Ph\(_3\)P, Ph\(_2\)S and Ph\(_3\)N have similar spectra.

Moreover, the deep colours of aromatic phosphide ions e.g.

show the presence of strong conjugation. Recently Gallagher and Mann\(^4\) have reported the polycyclic derivative (I) which becomes highly coloured on protonation (II).

(ii) The following kinetic evidence suggests that $p_{\pi}-p_{\pi}$ bonding can stabilize the transition state\(^5\) of some phosphorylations. Normally these reactions are bimolecular\(^5\):

and the rate increases with the positive charge on the phosphorus\(^5\) atom as shown by the rate sequence\(^6\) for the hydrolyses,

The bonding and stereochemistry of these reactions will be considered in a later section.
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

The following rate sequence is however frequently observed,7,

\[
\begin{align*}
\text{(III)} & \\
\text{(IV)} & \\
\text{(V)} & \\
\end{align*}
\]

where the reactions of (III) and (IV) are bimolecular. The high reactivity of the dianion (V) indicates a unimolecular mechanism,

\[
\begin{align*}
\text{O} & \text{P} & \text{O} \\
\text{O} & \text{P} & \text{O} \\
\text{O} & \text{P} & \text{O} \\
\end{align*}
\]

Similarly derivatives of phosphoramidic acids are very reactive in dilute alkaline solution,8, suggesting the following mechanism.

\[
\begin{align*}
\text{RHN} & \text{P} & \text{O} \\
\text{RHN} & \text{P} & \text{O} \\
\text{RHN} & \text{P} & \text{O} \\
\end{align*}
\]

The intermediate \( \text{PO}_3^- \), which is analogous to \( \text{NO}_3^- \), may be stabilized by \( d_n \) bonding using hybridized \( d_{xy} \) and \( d_{yz} \) orbitals (Figure 4).

\[
\begin{align*}
\text{Figure 4. Possible } p_x - p_x \text{ and } d_n - p_n \text{ bonding in the } \text{PO}_3^- \text{ ion}
\end{align*}
\]

This mechanism explains† the anomalous reactivity of monophosphates9 in the pH range 4–5, where the concentration of the singly ionized form \( \text{RO(OH)}\text{PO}_2^- \) is a maximum. It should be stressed however that in spite of intensive work for several years, no direct evidence for these intermediates has been obtained.

TRIVALENT PHOSPHORUS COMPOUNDS

The electronic configuration \( 3s^2 \ 3p^3 \) and the large difference in energy of the \( s \) and \( p \) levels (Figure 1) lead to the formation of \( 3p \) bonds, as in amines.

† This mechanism may also explain geminal substitution in the reactions of the phosphonitrilic halides (phosphazenes).
The $\overline{\chi}$PX angles increase from 93° in phosphine to 99° in Me$_3$P, whereas values for the corresponding amines are close to the tetrahedral angle (107° and 108° respectively). The recent preparation of optically active phosphines by Horner et al.$^{10}$ shows that the inversion frequency is very low compared with that of ammonia.

Phosphines have a strong tendency to donate the $3s$ electrons in a wide range of nucleophilic reactions, owing to (i) the relatively low ionization potential ($\sim$10 eV for PH$_3$) and (ii) the formation of strong $sp^3$ bonds stabilized by ionic forces. The basicity of aliphatic phosphines is highly dependent on the alkyl substituent$^{11}$, whereas the $pK_a$'s of the corresponding amines are approximately constant. This difference has been attributed$^{12}$ to the changes in hybridization on formation of the $sp^3$ hybridized phosphonium ion. As already mentioned the bond angles in NH$_3$ are close to the tetrahedral angle, so that almost no promotional energy is required to reach the $sp^3$ state. A greater promotional energy is required for phosphine than for Me$_3$P since the angles are considerably different, resulting in a large difference in $pK_a$.

This explanation ignores differences in solvation energies, and approximate calculations$^{13}$ suggest that the energies of protonation of phosphine and ammonia are similar in the gas phase ($\sim$209 and $\sim$207 kcal/mole respectively). The large difference in $pK_a$ may therefore be due to the greater solvation energy of NH$_4^+$ since the radius of the PH$_4^+$ ion is ca. 0.4 Å greater than that of the NH$_4^+$ ion. By comparison with known solvation energies of ions of similar radii, this would account for about 20 kcal/mole. Also the solvation energies of Me$_3^+$PH and Me$_3$NH should be similar, leading to similar $pK_a$ values.

Some of the most important reactions in organo-phosphorus chemistry involve the reactions of phosphines and phosphites with alkyl halides, e.g.

$$R_3P + R'CH_2X \xrightarrow{k} R_3P^-CH_2R' + X^- \xrightarrow{H^+} R_3P=CHR' + HX$$

(VI)

Now for a closely related series of nucleophiles the value of log $k$ increases with $pK_a$, and hence we have the reactivity sequence$^{14}$ $R_3P > R_2PH >$ RPH$_2 >$ PH$_3$.

In contrast, the reactivity of amines changes in the reverse order, and is controlled by steric hindrance as discussed in detail by H. C. Brown$^{15}$.  

<table>
<thead>
<tr>
<th>$\overline{pK_a}$</th>
<th>NH$_3$</th>
<th>MeNH</th>
<th>Me$_3$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>N angle</td>
<td>9.25</td>
<td>10.64</td>
<td>10.72</td>
</tr>
<tr>
<td>107°</td>
<td>108°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P angle</td>
<td>$-14^\circ$</td>
<td>~0</td>
<td>3.9</td>
</tr>
<tr>
<td>93.0°</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

Steric hindrance also modifies the reactivity of phosphines as shown by the data\textsuperscript{14} plotted in Figure 5.

![Graph showing the relation between log k and pKa for the reactions between phosphines and ethyl iodide; the full lines represent the electronic effect and the dotted lines the steric effect.]

Phosphines are very reactive towards centres of high electron density \textit{e.g.} oxygen and halogens, as shown by the following reactions\textsuperscript{16}, and in this way differ from the corresponding amines,

\[
\text{R}_3\text{P} + \text{Ph'C-O-O-C'Ph} \rightarrow \text{Ph'C-O-O-C'Ph} \rightarrow +\\
\text{Ph'C} + \text{Ph'CO'O-CO'Ph}
\]

and\textsuperscript{17}

\[
\text{R}_3\text{P} + \text{Br'CH}_2\text{--COR} \rightleftharpoons \text{R}_3\text{P}^{\dagger} \text{Br} \rightarrow \text{R}_3\text{P}^{\dagger}\text{O-C} \rightarrow \text{R}_3\text{P}^{\dagger}\text{CH}_2\text{COR} \rightarrow \text{R}_3\text{P}^{\dagger} \text{Br}^{-}
\]

This difference may be attributed to reduced inter-electronic repulsion energy and greater polarizability of a phosphine compared with an amine, which prefers to react at electron-deficient centres. This difference in nucleophilic behaviour between first and second row elements \textit{cf.} R\textsubscript{3}N and
THE IMPORTANCE OF $d$-ORBITALS

The $d$ orbitals of an uncharged phosphorus atom are too diffuse for significant overlap with $p_{\sigma}$ or $p_{\pi}$ orbitals. A formal positive charge however contracts the $3d$ orbitals which become commensurate with other orbitals (Figure 6).

![Figure 6. $d_\sigma-p_\sigma$ (VII) and $d_\pi-p_\pi$ (VIII) bonding](image)

This is shown by the change in overlap integral $S_{ab}$ with formal positive charge on the phosphorus atom (Figure 7). As already pointed out however, the $3s \rightarrow 3d$ promotional energy is very high, and the calculations of

![Figure 7. Overlap integrals for $3p_\sigma-3d_\sigma$ as functions of $t (= \frac{1}{2}(\alpha_A - \alpha_B)/(\alpha_A + \alpha_B))$ with several values of $p (= \frac{1}{2}(\alpha_A + \alpha_B)r)$ where $\alpha_A = Z_A/n_A$ ($Z_A$ is the effective atomic number of A and $n_A$ the effective principal quantum number of atom A) and $r$ is the internuclear distance in Bohr units](image)

Craig and Magnusson suggest that this may increase with charge on the phosphorus atom. (This is also suggested by the large energy difference $3s^23p^2 \rightarrow 3s^23p^23d$ and $3s^23p^2 \rightarrow 3s^23p^3d$ although this may be due to differences in $3p$ electronic repulsion). The contribution of $3d$ orbitals to the total bonding is therefore relatively small. The experimental evidence for $d$-orbital participation will now be reviewed.

$d_\pi-p_\pi$ BONDING

Physical evidence rests mainly on (a) high bond energies (see Table 3), and (b) small bond distances in $P=O$ and $P=S$ compounds. Also the
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

Bond moments\(^{24}\) of amine oxides are greater than those of the corresponding phosphinoxides, leading to the following estimates of charge distribution in the P=O and N→O bonds.

\[
\begin{align*}
0.4^+ & \quad 0.4^- \\
P & \quad O \\
0.7^+ & \quad 0.7^- \\
N & \quad O
\end{align*}
\]

<table>
<thead>
<tr>
<th><strong>Compound</strong></th>
<th><strong>D(P=O)</strong></th>
<th><strong>Compound</strong></th>
<th><strong>D(P=O) or D(P=S)</strong> (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(<em>5)O(</em>{10})</td>
<td>138</td>
<td>(EtO)(_3)PO</td>
<td>151</td>
</tr>
<tr>
<td>Eu(_3)PO</td>
<td>130</td>
<td>(PrO)(_3)PO</td>
<td>146</td>
</tr>
<tr>
<td>Cr(_2)PO</td>
<td>128</td>
<td>(Me(_2)N)(_3)PO</td>
<td>139</td>
</tr>
<tr>
<td>Fe(_3)PO</td>
<td>125</td>
<td>(Et(_2)N)(_3)PO</td>
<td>156</td>
</tr>
<tr>
<td>M(_2)PO</td>
<td>139</td>
<td>(EtO)(_3)PS</td>
<td>90-6</td>
</tr>
<tr>
<td>Pr(_5)PO</td>
<td>138</td>
<td>Pr(_3)PS</td>
<td>91-6</td>
</tr>
<tr>
<td>Bu(_3)PO</td>
<td>137</td>
<td>Bu(_3)PS</td>
<td>91-5</td>
</tr>
<tr>
<td>Ph(_3)PO</td>
<td>128</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since phosphorus is more electronegative than nitrogen, the reverse order is to be expected if \(\sigma\)-bonding alone is used, and the relatively low P=O bond polarity suggests \(\pi\)-bonding. Within recent years however the interpretation of bond properties in conjugated organic molecules has been heavily criticized since changes in \(\sigma\)-bond hybridization, and electronegativity differences are neglected\(^{25}\). These criticisms are even more valid for phosphorus compounds. The \(d_{\pi}p_{\pi}\) bonds are necessarily highly polar (see structure VIII), and the difference between the NO and PO bonds may be due to electrostatic factors as suggested by Pitzer\(^{26}\). He considers the greater bond energies of second row elements compared with first row elements to be due to (i) reduced valency shell repulsions, thus permitting a relatively closer approach of the bonding atoms before inner shell repulsions become important and (ii) the resulting large electrostatic interactions. A similar argument based on the greater polarizability of phosphorus than nitrogen could be used. This conclusion is supported to some extent by the complete absence of spectroscopic evidence in favour of \(d_{\pi}\) bonding. The u.v. spectra of phosphoryl compounds show no \(n-\pi^*\) transitions\(^8\), characteristic of carbonyl compounds, and the ion PO\(_4^{3-}\) like SO\(_4^{2-}\) is transparent\(^{27}\) up to at least 7-8 eV (contrast MnO\(_4^{-}\), CrO\(_4^{2-}\)). Recently, however, Griffin\(^{28}\) has found the spectra of tri-2-pyrrylphosphine oxide and the \(N\)-methyl analogue to be similar to that of the corresponding \(\alpha\)-ketone.

**Infrared spectra**\(^{29}\) give no strong support for \(d_{\pi}p_{\pi}\) bonding. Thus, phenyl and amino groups increase \(\nu_{P=O}\) whereas they decrease \(\nu_{C=O}\). However when the values of \(\nu\) for both series are related to the electronegativities of the groups attached to the phosphorus and carbon atoms, electron-donating groups (Ph, NR\(_3\), OR) reduce the frequencies in both cases (Figure 8). The strong inductive effect of aromatic groups is reflected in reactivity and basicity. Thus esters of phenyl phosphonic acid undergo alkaline hydrolysis.
more rapidly than esters of alkylphosphonic acids\textsuperscript{30} in contrast to the corresponding carboxylic acid esters, and Bestmann\textsuperscript{31} has recently shown that the aromatic phosphonium salt (IX) is considerably more acidic than the aliphatic analogue (X).

\[
\begin{align*}
\text{Ph}_3\text{P}—\text{CH}_2—\text{C}^=\text{O} & & \text{(IX)} \\
(C_6\text{H}_{11})_3\text{P}—\text{CH}_2—\text{C}^=\text{O} & & \text{(X)}
\end{align*}
\]

Chemical evidence for \(d_{\pi}-p_{\pi}\) bonding rests mainly on the effect of substitution on the reactivity of phosphoryl compounds and on the stability of phosphine methylenes relative to the corresponding nitrogen compounds\textsuperscript{32}, in particular the isolation of stable phosphobetaines\textsuperscript{33} (from IX and X). A quantitative measure of the influence of \(d_{\pi}-p_{\pi}\) bonding is given by the rate of hydroxide ion catalysed exchange of the protons of quaternary phosphonium and similar cations\textsuperscript{34}.

The rate data for the following and similar reactions,

\[
\begin{align*}
\text{Me}_3\text{P}^+—\text{CH}_3 + \text{OH}^- & \xrightarrow{k} \text{Me}_3\text{P}=\text{CH}_2 + \text{H}_2\text{O} + \text{D}_2\text{O} \\
\text{Me}_3\text{PCH}_2\text{D} + \text{DO}^- & \rightarrow \text{Me}_3\text{P}=\text{CH}_2 + \text{H}_2\text{O}
\end{align*}
\]

are given in the following \textit{Table 4}.

\begin{table}[h]
\centering
\begin{tabular}{l|cccccccc}
\textbf{Central ion} & \textbf{N} & \textbf{P} & \textbf{As} & \textbf{Sb} & \textbf{S} & \textbf{Se} & \textbf{Te} \\
\textbf{log} \textit{k} & -9.75 & -3.37 & -4.61 & -5.62 & -2.44 & -4.09 & -4.63 \\
\end{tabular}
\end{table}
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

The colours of the phosphomethylenes (recently prepared in a pure state by Bestmann\textsuperscript{31}) give some indication of the magnitude of the $d_\pi$ contribution,

(XI) Ph$_3$P=CH$_2$ (orange); (XII) Ph$_3$P=CPh$_2$ (deep red); (XIII) (C$_6$H$_{11}$)$_3$P=CH$_2$ (v. pale yellow); (XIV) Ph$_3$P=CHCOR (colourless).

This (admittedly limited) data is consistent with an excitation from a non-bonding $p_\pi$ orbital of CH$_2$ to an accessible 3$d$ level or from a $p_\pi$–$d_\pi$ bonding to a $p_\pi$–$d_\pi$ antibonding orbital. The increase in colour from (XI)–(XII) could be due to greater conjugation in the $\pi$ system (compare benzene and anthracene), and the absence of colour of (XIV) to the localization of the electrons in the CHCOR group thus increasing the excitation energy. The increase in colour from (XIII) to (XI) could be due to the conditional stability of the 3$d$ level by the inductive effect of the phenyl groups, which would reduce the excitation energy. This interpretation is of course speculative, and further spectroscopic studies are highly desirable.

$d_\sigma$–$p_\sigma$ Bonding is usually invoked to explain the stability of compounds with higher coordination numbers, although the same criticism based on the high promotional energy holds. Thus a partial ionization of the electrons to give a positively charged phosphorus atom results in the following resonance hybrid (Pauling\textsuperscript{35}),

$$\text{PX}_5 \leftrightarrow ^+\text{PX}_4^-$

For this reason, electronegative substituents stabilize the higher valency states (Table 5), and the bonds probably have considerable partial ionic character.

<table>
<thead>
<tr>
<th>Electroneg. (Pauling)</th>
<th>2.8</th>
<th>2.8</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{PX}_5</td>
<td>PPh$_3^*$</td>
<td>PBr$_5$</td>
<td>PCl$_5^*$</td>
<td>P(OR)$_5^*$</td>
<td>PF$_5^*$</td>
</tr>
<tr>
<td>\text{PX}_6</td>
<td>PCl$_5^-$</td>
<td>P(OR)$_5^-$</td>
<td>P(OR)$_5^-$</td>
<td>P(OR)$_5^-$</td>
<td>PF$_5^-$</td>
</tr>
</tbody>
</table>

* discussed in detail by Ramirez\textsuperscript{36} (pages 337–370).
+ Allecock\textsuperscript{37} recently described the tris catecholate.

The interest here is mainly in the stereochemistry of the 5-coordinated structures, since several alternative hybridizations are possible. Group theory predicts a bipyramidal configuration\textsuperscript{38}, which has been confirmed in several cases (marked by an asterisk in Table 5). The bipyramidal structure poses difficult questions of bond symmetry. For example, if all the bond lengths are equal (as assumed by Duffey\textsuperscript{39} in a treatment of the angular functions only of the kind developed by Pauling\textsuperscript{35}), then the axial bonds are stronger than the radial bonds (see the discussion on Westheimer’s transition state\textsuperscript{40}). On the other hand, assuming complete $sp^3d$ hybridization to give bonds of equal energy (e.g. Craig \textit{et al.} used equal overlap\textsuperscript{19}) the axial bonds are longer than the radial bonds (as observed in PCl$_5$ and PF$_5$). In an alternative structure (as in an $S_N2$ transition state) the axial $pd$ bonds may be weaker than the equatorial ($sp^2$) bonds.
R. F. HUDSON

Other possible forms of hybridization, e.g. (XV) and (XVI) (see Figure 9) are possible. Structure (XV) could be stabilized by hybridization with $d_2^2$ and $d_{x^2-y^2}$ orbitals, and electrostatic calculations suggest that the difference in energy between the bipyramidal and square planar (XV) structures is small (the optimum $X\hat{P}X$ angle in (XV) is greater than $100^\circ$).

\[ \begin{array}{c}
\begin{array}{c}
\text{(XV)} \\
\text{(XVI)}
\end{array}
\end{array} \]

Figure 9. Possible $sp^3d$ hybridized structures

Structure (XV) has recently been confirmed for SbPh$_5$ in the solid state, but Ph$_5$P and Ph$_5$As adopt the bipyramidal structure.

Gillespie has suggested that hybridization of one $sp^3$ and a $d_{xy}$ orbital gives an alternative structure (XVI) with comparable energy to the others. Support for this structure comes from the high reactivity of the bicyclic silicon compound (XVII), which is in contrast to the inactivity of the carbon analogue. Similar compounds of phosphorus have recently been prepared but so far no reactivity studies have been reported.

\[ \begin{array}{c}
\begin{array}{c}
\text{(XVII)} \\
\end{array}
\end{array} \]

Information on the relative importance of these structures has come from recent investigations with optically active phosphorus compounds. Thus we have demonstrated that the following reactions proceed with 100 per cent inversion of configuration:

\[ \text{RO}^- + \text{R}_2\text{P}(\text{OR})^* \rightarrow \text{RO} \text{PO} \text{R}_2 \text{R}_1 + [\text{R}^*\text{O}]^- \]

and

\[ \text{HO}^- + \text{R} \text{SP} \text{R} \rightarrow \text{H}_2\text{O} \rightarrow 2 \text{RO} \text{POS} \text{OH} \]

The mechanism is thus similar to an $S_N2$ displacement on a saturated carbon atom (which always proceeds by a Walden inversion), and the transition state is bipyramidal, like PF$_5$, PCl$_5$ and PPh$_5$.

A transition state of this structure, where the axial and radial bonds are not equivalent also explains the absence of $^{18}\text{O}$ exchange in such reactions.
Similarly the reaction of hydroxide ions with phosphonium salts according to the following mechanism proceeds with 100 per cent inversion of configuration:

\[
\begin{align*}
\text{R}_1\text{P}^+\text{R}_2\text{CH}_2\phi + \text{HO}^- & \rightarrow \text{HO}^-\text{P}^-\text{CH}_2\phi \\
\text{HO}^-\text{P}^-\text{CH}_2\phi & \rightarrow \text{HO}^-\text{P}^-\text{CH}_2\phi + \text{OH}^- \\
\text{HO}^-\text{P}^-\text{CH}_2\phi + \text{H}_2\text{O} & \rightarrow \text{R}_1\text{R}_2\text{R}_3
\end{align*}
\]

It appears therefore that bimolecular displacements normally proceed through bipyramidal intermediates.

In cyclic processes however, this is not the case. Thus the Wittig reaction with benzaldehyde, which proceeds through an intermediate betaine, and which is now known to be rapid, (when non-complexed), involves complete retention of configuration, so that the forming bond and breaking bond are at an angle of ca. 90°, according to the transition state (XVIII).

\[
\text{(XVIII)}
\]

The analogous reactions of phosphonate ions (XIX), and phosphinimines (XX) probably proceed via similar cyclic transition states, viz.

\[
\text{(XIX)} \quad \text{and} \quad \text{(XX)}
\]

The favourable energetics provided by spd bonding mean that many such re-arrangements, which are impossible in carbon and nitrogen chemistry can rapidly occur, e.g. the following re-arrangement:
which might have a bearing on the mechanism of the Perkow reaction since it is an alternative to direct attack on carbonyl oxygen;

The importance of \( d \) orbitals in the radial bonds is also suggested by the work of Haake and Westheimer with the highly reactive ethylene phosphates. In alkaline solution exclusive ring opening is observed, but in acid solution a mixture of cyclic and linear dialkyl phosphates is obtained as follows,

The very high reactivity of these cyclic phosphates is due to ring strain which is released on formation of the transition state. The cyclic O–P–O angle is thus the same in the transition states of the two reactions, which differ only in the position of the proton. In view of the tendency of phosphorus to adopt small angles, this cyclic angle is assumed to be 90°. Westheimer
CHEMICAL BONDING IN ORGANO-PHOSPHORUS COMPOUNDS

further assumes that the making and breaking bonds are symmetrical, and therefore favours structure (XI) or (XII).

\[
\text{(XI)} \quad \begin{array}{c}
\text{MeO} \\
\text{H_2} \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{CH}_2 \text{CH}_2 \\
\text{O} \\
\text{H}^+ \\
\text{O} \\
\end{array}
\quad \begin{array}{c}
\text{H}^+ \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{MeO} \\
\text{H}_2 \\
\text{O} \\
\text{H}^+ \\
\end{array}
\quad \text{or}
\quad \begin{array}{c}
\text{MeO} \\
\text{H}^+ \\
\text{O} \\
\text{P} \\
\text{O} \\
\text{H}_2 \\
\text{O} \\
\text{H}^+ \\
\end{array}
\]

\[
\text{(XII)}
\]

In view of our previous discussion however, in an \( sp^3d \) hybridized system, the relative energies of the various bonds cannot be readily ascertained. Therefore, although the above results suggest that \( d^1 \) bonds are used in the transition state (3 equivalent bonds), the exact structure is not established.

In conclusion we may note that phosphorus chemistry is largely the chemistry of heteropolar \( \sigma \)-bonds. The present interest in the organic chemistry of phosphorus and other non-metallic and metalloid elements, together with the recent discussion of the importance of hybridization on the strengths of \( \sigma \)-bonds in conjugated organic molecules have greatly stimulated theoretical work on the nature and description of single bonds. Considerable advances in the theoretical treatment of \( \sigma \)-bonds, comparable to the advances produced by the molecular orbital treatment of conjugated molecules are expected within the next few years.

References

   3574.
    332;
R. F. HUDSON

27 C. Klixull-Jørgensen. Private communication;
31 H. J. Bestmann. Private communication.
32 G. Wittig and G. Geissler. *Ann.* **580**, 44 (1953);