Twenty-five molecules of organophosphorus compounds (OPC) of the \((XY)PO\) type (where \(X, Y, Z = R, OR, SR, NR_2, F\)) were calculated by the simple molecular-orbital method. The results explained certain experimentally-observed details of the mechanisms underlying the reactions of OPC with nucleophilic and electrophilic reagents. The calculated energies of the lower unoccupied orbitals and the nucleophilic superdelocalizabilities of the phosphorus atom were also compared quantitatively with the velocity constants and activation energies of the alkaline hydrolysis of various fluoroanhydrides of phosphorus-containing acids. A quantitative relationship was established between the sum of the inductive Taft constants of the \(X, Y, \) and \(Z\) substituents and the total energy of the \(\pi\) system of the OPC molecule. A relation was also established between the resonance energy and the sum of the orders of the bonds in the OPC molecule, on the one hand, and the value of the chemical shift of the \(^{31}\)P nucleus in the NMR spectrum on the other.

**Calculation of the Fourfold-Coordinated Phosphorus Molecules by the Molecular-Orbital Method**

The literature contains relatively few papers [1-8] relating to the calculation of phosphorus compounds with \(P=O\) bonds by the method of molecular orbitals; the number of molecules which have been considered is extremely limited, and the choice of parameters used for the calculation has not always been of the best. We therefore used the \(\pi\) electron approximation of Hückel in order to calculate 25 molecules of the

\[
\begin{array}{c}
\text{O} \\
\mid \\
\text{P} \\
\downarrow \\
\text{X} \\
\mid \\
\text{Y} \\
\uparrow \\
\text{Z}
\end{array}
\]

(1)
type with \(X, Y, Z = R, OR, SR, NR_2, F\). We assumed that the phosphorus atoms and the phosphoryl oxygen each introduced one electron into the \(\pi\) system [1, 3], the ester oxygen, nitrogen, and fluorine atoms introducing an unshared pair of \(p\) electrons; hyperconjugation of the saturated hydrocarbon radicals was not considered. In the case of the thio-ester group, allowance was made for the conjugation of the central phosphorus atom with the unoccupied \(d\) orbital of the sulfur atom. This approach provided an explanation for a number of facts earlier unexplained when considering the conjugation of the electron of the phosphorus atom with the unshared pair of \(p\) electrons of the sulfur atom, for example, the high rate of hydrolysis of fluoroanhydrides of type (1) containing an \(SR\) group, the values of the chemical shifts of the \(^{31}\)P nucleus in the NMR spectra, and so on.

The Coulomb \((\alpha_A)\) and resonance \((\beta_{AB})\) integrals needed for the calculation (Table 1) were calculated by the Rasch method [9].

TABLE 1. Parameters Used for the Calculation

<table>
<thead>
<tr>
<th>Atom</th>
<th>( I, \text{ eV} )</th>
<th>( r_{PX}, \text{ Å} )</th>
<th>Literature cited</th>
<th>( h_X )</th>
<th>( s_{PX} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>17.28</td>
<td>1.54 ( \uparrow )</td>
<td>[15, 19]</td>
<td>1.83</td>
<td>0.90 ( (a) ) 0.97 ( (b) )</td>
</tr>
<tr>
<td>N</td>
<td>14.12</td>
<td>1.67 ( \uparrow )</td>
<td>[20, 21]</td>
<td>0.51</td>
<td>0.85</td>
</tr>
<tr>
<td>S</td>
<td>17.70</td>
<td>1.56 ( \uparrow )</td>
<td>[22]</td>
<td>2.00</td>
<td>0.90</td>
</tr>
<tr>
<td>F</td>
<td>20.86</td>
<td>1.50 ( \uparrow )</td>
<td>[15]</td>
<td>3.33</td>
<td>0.87</td>
</tr>
</tbody>
</table>

\( * (a) \) for \( I_p = 11.64 \text{ eV}; \) (b) for \( I_p = 5.0 \text{ eV}. \)
\( \uparrow \) in fluoroanhydrides.
\( \uparrow \) in molecules not containing any fluorine atom.

\[ g_A = \alpha + h_A \beta; \quad \beta_{AB} = k_{AB} \beta, \]  

(2)

where

\[ h_A = \frac{I_A - 5.40}{2.39} \quad k_{AB} = \frac{0.2275 (I_A + I_B) S_{AB}}{I_A + S_{AB}}. \]  

(3)

Here \( I \) is the ionization potential of a particular atom in the corresponding valence state; \( S_{AB} \) is the overlap integral of the \( \pi \) orbitals of the A and B atoms. The values of \( I \) were taken from [10] and \( S_{AB} \) for the experimentally-observed interatomic distance \( r_{AB} \) (Table 1) from [11-13]. The effective nuclear charges required for finding the overlap integrals in the case of the p orbitals were calculated from Slater's rules (see, for example, [13]) and in the case of the d orbitals from the rules proposed in [13].

In order to calculate the Coulomb and resonance integrals we took two values of the ionization potential of the phosphorus atom: (a) \( I = 11.64 \text{ eV} \) for the \( \pi \) electron in the \( t_2^2t_1^2t_0^1t_1^1 \) state and (b) \( I = 5.0 \text{ eV} \) for the d electron. The ionization potential \( I = 11.64 \text{ eV} \) leads to the value \( h_P = -0.53 \), close to the values of \( h_P \) used by other authors [1-5]. However, the value of \( I = 5.0 \text{ eV} \) (\( h_P = -3.31 \)) is better based physically: the valence angles in the compounds of fourfold-coordinated phosphorus are close to tetrahedral [15], i.e., \( sp^3 \) hybrid orbitals should take part in the \( \pi \) bonds; then only the d electron of the phosphorus atom can take part in the \( \pi \) system. The calculations of the OPC molecules using parameters (a) and (b) led to the same laws of variation for various quantities in the specified series of compounds; however, in the case of \( I = 11.64 \text{ eV} \) the relationships were in a number of cases more explicit.

In the case of the sulfur atom, the energy of the d orbital \( (I_d) \) was calculated from the ionization potential of the p electron in the \( sp^3pp \) state \( (12.39 \text{ eV} \) [10]) and the energy of the p-d transition \( (\Delta I): I_d = I_p - \Delta I \).

According to the calculations of various authors, the value of \( \Delta I \) is 7.21 [16], 7.35 [17], and 8 eV [18]; an experimental value of \( \Delta I = 8.38 \text{ eV} \) was also given in [16], and this we used for calculating \( I_d \).

The solution of the secular determinants was carried out on the Minsk-2 computer.

Reactions of OPC with Nucleophilic and Electrophilic Reagents

In comparing the results of the calculation with experimental data relating to the reactivity of compounds of type (1), we used the so-called electrophilic \( (M^E) \) and nucleophilic \( (M^N) \) superdelocalizabilities [23] of various atoms of the OPC molecules: