Acknowledgments. The authors thank Mr. William Jorgensen for computational assistance. The services of the Princeton University Computer Center (supported in part by National Science Foundation Grants No. GJ34 and GU3157) are appreciated. One of us (P. A. K.) thanks the NSF for fellowship support. Helpful comments by the referees are acknowledged.

Kraemer and Diercksen [*Chem. Phys. Lett.*, **5**, 463 (1970)] carried out an SCF calculation on the sp^2 configurations of the $H_5O_2^+$ system with an extended basis set of lower total energy than ours ($E_t = -152.43$), but found essentially the same energy for the reaction $H_3O^+ + H_2O \rightarrow H_5O_2^+$ (32.2 kcal/mol) in addition to an extremely shallow proton well at the minimum 0–0 separation (2.39 Å). DePaz, Ehrenson, and Friedman [*J. Chem. Phys.*, **52**, 3362 (1970)] studied a number of hydrated ions ($H_{2n+1}O_n^+$ and $H_{2n-1}O_n^-$) by CNDO/2 molecular orbital methods. Their minimum energy structure for $H_5O_2^+$ was similar to ours, but they carried out a much more complete search. The computed reaction energies were too high, and the authors proposed a semiempirical procedure to scale the results to fit experimental data.

Noble and Kortzeborn [*ibid.*, **52**, 5375 (1970)] studied the HF_2^- ion as well as HF_2 and HeF_2 by LCAO–MO techniques. These authors, using a basis set intermediate between ours and the best basis set of McLean and Yoshimine,[12b] found an energy of reaction of 40 kcal for $F^- + HF \rightarrow HF_2^-$ as well as estimating a lower limit of 28 kcal from McLean and Yoshimine's results. They compared their results to a more recently obtained experimental value of 37 kcal: S. A. Harrell and D. H. McDaniel, *J. Amer. Chem. Soc.*, **86**, 4497 (1964). It should be noted that our dimerization energy (52 kcal/mol) is not in as good agreement with this value. The contrast between $H_5O_2^+$ (where different basis sets give similar reaction energies) and HF_2^- (where the theoretical values differ substantially) is a further example of the fact that Hartree–Fock calculations treat positive ions much more successfully than negative ions.

Noble and Kortzeborn also fit their data to the four-term potential suggested by Ibers[9] in his spectroscopic study of HF_2^-. In Table V we calculated K_s (the symmetric stretch force constant) by fitting the $D_{\infty h}$ FHF^- structures to a parabola near the minimum, and K_a (the asymmetric stretch force constant) by fitting the R(F–F) = 4.25 au points to a parabola *after* subtracting off the quartic term reported by Ibers.[9] We have now fit our energy points to the same four-term potential used by Noble and Kortzeborn [$V = K_sQ_s^2 + K_aQ_a^2 + aQ_a^4 + bQ_a^2Q_s$; $Q_a \equiv {}^1/_2(r\text{HF} - r\text{HF}')$; $Q_s = (r\text{HF} + r\text{HF}')$], and the results of all the HF_2^- force field calculations are given in Table VII.

Two additional points deserve mention. First, Noble and Kortzeborn compared their calculations to Ibers'[9] original results [*J. Chem. Phys.*, **41**, 25 (1964)], which were later corrected [*ibid.*, **48**, 539 (1968)]. Secondly, Noble and Kortzeborn used a different definition for the asymmetric stretching normal mode (by a factor of 0.5), so the Ibers' force constants[9] have been adjusted by the following factors ($K_s = {}^1/_2 K_1$; $K_a = 2K_3$; $a = 2K_4$; $b = 1/\sqrt{2} K_{13}$) in order to compare them with the calculated values from the molecular orbital studies. The conclusions from this are similar to those of Noble and Kortzeborn, *i.e.*, none of the SCF calculations is in especially good agreement with Ibers' results. Also, the results do not improve with an extension of the basis set—the highest total energy calculation (ours) appears to give the best agreement with Ibers' values. This is a rather discouraging result, but is not without precedent. A single Slater basis predicts a dipole moment for H_2O of 1.82 D, and the lowest energy calculation predicts 1.99 D (experimental, 1.84 D).

We have also attempted to fit our $H_5O_2^+$ results to the same four-term potential with much less success (see Table VII). In that system, the external hydrogens must contribute significantly to the normal modes, and we have not varied any of the external O–H distances.

An LCAO MO SCF Study of "p_π–d_π" Bonding to Phosphorus. The H_3PO Molecule

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Abstract: SCF calculations were carried out for the hypothetical compound phosphine oxide, H_3PO. The effect was studied of adding either a d or another p orbital to a phosphorus atom depicted in terms of seven s and three p Gaussian orbitals. The added p orbital gave a considerably greater improvement in total energy than did the d because the added p contribution was particularly large in phosphorus inner shells. However, introduction of the d orbital led to a large change in the electronic population of the two highest filled molecular orbitals. Population analysis showed that a major part of this change can be attributed to p_π–d_π bonding, and that introduction of d character to the molecule leads to an overall loss of *ca.* 0.1 electron charge from the oxygen and a gain of *ca.* 0.5 electron by the phosphorus, with the difference being made up by the hydrogens. Three-dimensional plots of electron densities across the H–P–O plane are presented to illustrate the electronic structure of this phosphoryl compound.

The question of the role of outer d electrons in the bonding of second-row atoms such as silicon, phosphorus, and sulfur is still a subject of dispute.[2,3] Although a considerable body of experimental data is readily interpreted in terms of the concept of p_π–d_π bonding involving the d orbitals of these atoms, and although semiempirical investigations of the importance of d orbitals in the binding of second-row elements have been made by Brown and Peel,[4] using the VESCF method, and by Santry and Pople (CNDO),[5] the only nonempirical study of which we are aware is by Boyd and Lipscomb[6] whose LCAO SCF results for PO and PO^- show a large contribution of phosphorus 3d orbitals to bonding. An approximate model of phosphine oxide based on the valence bond method has also been published.[7]

In order to shed further light on this matter, we have carried out the preliminary LCAO MO SCF studies[8]

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(1) To whom communications concerning this paper should be addressed at Vanderbilt University.

(2) C. A. Coulson, *Nature* (*London*), **221**, 1106 (1969).

(3) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(4) R. D. Brown and J. B. Peel, *Aust. J. Chem.*, **21**, 2589, 2605, 2617 (1968).

(5) D. P. Santry and G. A. Segal, *J. Chem., Phys.*, **47**, 158 (1967).

(6) D. R. Boyd and W. N. Lipscomb, *ibid.*, **46**, 910 (1967).

(7) K. A. R. Mitchell, *Can. J. Chem.*, **46**, 3499 (1968).

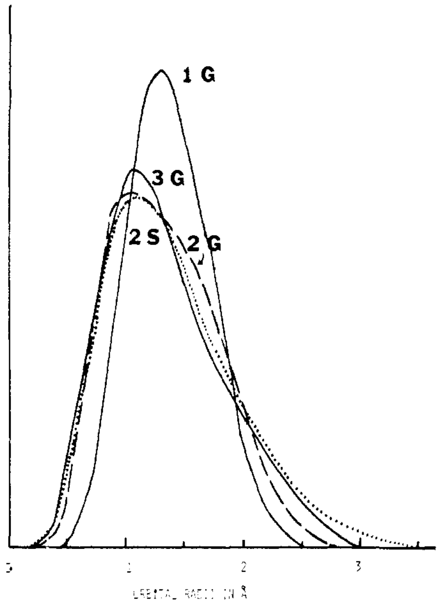

Figure 1. Radial density plots of the 3d orbital of the P^+ ion for the ^5F term of the sp^2d configuration. The dotted line (2S) corresponds to the use of two Slater-type orbitals to describe the 3d electron. The dashed line (2G) corresponds to the use of two Gaussian orbitals and the solid line labeled 3G to three Gaussian orbitals. The tallest curve (1G) shows the radial distribution function corresponding to the use of a single Gaussian orbital to represent the 3d electron.

reported below for the hypothetical molecule phosphine oxide, H_3PO. This compound was chosen as having the lowest number of molecular orbitals for a phosphoryl structure and hence being describable in terms of a linear combination of a relatively small number of atomic orbitals in an SCF calculation. By using s- and p-orbital exponents which were atom optimized and then optimizing the d-orbital exponent in the molecule, it was felt that this investigation would answer two important questions, the first being whether or not the postulated p_π–d_π bonding could be dissected out of the delocalized orbitals resulting from an SCF calculation; and the second being whether this effect (if detectable) would show up in a rather limited basis-set description.

Calculational Details

The LCAO MO SCF calculations reported herein were made with the program MOSES.[9] Planar electron density maps were obtained from one program[10] and converted to a three-dimensional representation by another.[11] SCF calculations on atoms were made with the program ATOM-SCF.[12]

Atom-optimized orbital exponents for phosphorus obtained from the latter program[12] and used in this work are shown in Table I. In order to estimate whether or not a single Gaussian exponent would give a reasonably meaningful representation for the d orbital, atom optimization of this orbital with frozen s and p orbitals was also carried out on a 731, a 732, and a 733 basis[13] for the phosphorus atom bearing a single positive charge in the sp^2d configuration.[14] A radial distribution plot of the d orbitals corresponding to the use of these basis sets and a Slater double-ζ set in describing the lowest energy spectroscopic term (^5F) of this P II configuration is shown in Figure 1, where it should be noted that the use of a single Gaussian d orbital gives a curve which is considerably less broad than the curves obtained by use of three Gaussian or two Slater orbitals. This means that the representation given herein for the d contribution to the radial part of the wave function is not a close approximation so that the related parameters (such as the overlap populations and mean radius of the optimized d orbital) will not be very accurate.

Table I. Exponents Employed for the s and p Gaussian Orbitals

Orbital type	P[a] $E = -338.1905$ au ($E = -339.9174$ au)	O $E = -74.2569$	H[b] $E = -0.3157$
s	4449	736.6	1.800
	670.6	112.9	0.2700
	157.3	26.04	
	43.21	7.212	
	13.34	0.5764	
	2.740		
	0.2036		
p	18.12 (47.00)	3.188	
	3.606 (10.34)	0.5764	
	0.2662 (2.692)		
	(0.2462)		

[a] The data for the 73 basis set are given first, followed in parentheses by those for the 74 set. [b] These exponents were chosen by extrapolation from values obtained by molecular optimization in H_2 and CH_4 (see C. J. Hornback, Ph.D. Thesis, Case Institute of Technology, 1967).

By comparing the measured bond angles and bond distances[15] for some phosphines and their respective phosphoryl derivatives, it was possible to estimate

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(8) This work was reported in part by J. R. Van Wazer at the International Colloquium on the Organic Chemistry of Phosphorus, Paris, May 1969 (*Bull. Soc. Chim. Fr.*, in press).

(9) L. M. Sachs and M. Geller, *Int. J. Quantum Chem.*, 1S, 445 (1967). Program MOSES consists of two versions, one using only s and p orbitals and the other allowing d orbitals. This program has undergone a number of minor modifications in our group by N. Winter, J. H. Letcher, and L. C. D. Groenweghe. It is always preceded by a program (written by J. H. Letcher) based on the mathematics described by J. H. Letcher and T. H. Dunning, *J. Chem. Phys.*, **48**, 4538 (1968), and in more detail by M. L. Unland, T. H. Dunning, and J. R. Van Wazer, *ibid.*, **50**, 3208 (1969). This introductory program calculates a starting set of coefficients from a localized-orbital, valence-bond description of the molecule, and thereby lessens considerably the number of iterations needed to achieve convergence in program MOSES and consistently assures successful convergence.

(10) W. E. Palke, an electron density plot program, later modified by T. H. Dunning at The California Institute of Technology and again changed by H. Marsmann in our laboratory.

(11) D. L. Nelson, "Perspective Plotting of Two-Dimensional Assays—PLOT3D, A Computer Program for a Digital Plotter," University of Maryland, Department of Physics and Astronomy, College Park, Md. 20742.

(12) B. Roos, C. Salez, A. Viellard, and E. Clementi, "A General Program for Calculation of Atomic SCF Orbitals," IBM Research Laboratories, San Jose, Calif. 95114.

(13) The notation used here to describe the size of a Gaussian basis set gives the number of s-type orbitals first, followed by the number of p-type and then the number of d-type orbitals. A slash separates the description of each atom, with the order being P/O/H. Thus 731/52/2 corresponds to the use of seven s, three p, and one d orbitals for the phosphorus, five s and two p for the oxygen, and two s for each hydrogen of the H_3PO molecule.

(14) For related Slater orbital calculations on the various configurations of neutral plus negatively and positively charged phosphorus atoms, see H. Marsmann, J. R. Van Wazer, and J.-B. Robert, *J. Chem. Soc. A*, 1566 (1970). Also see G. S. Chandler and T. Thirunamachandran, *J. Chem. Phys.*, **49**, 3640 (1968).

(15) L. E. Sutton, *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965. Also see D. E. C. Corbridge, *Top. Phosphorus Chem.*, **3**, 57 (1966).

Table II. Comparison of Energies (au) of Phosphine Oxide Calculated for Various Basis Sets

Energies	74/52/2 basis set	Difference ←	73/52/2 basis set	Difference →	731/52/2 basis set
Total electronic	−481.302	*−1.675*	−479.627	*−0.204*	−479.831
Orbital[a] $1a_1$	−80.136	*+0.202*	−80.338	*+0.028*	−80.310
$2a_1$	−20.587	*−0.020*	−20.567	*−0.057*	−20.624
$3a_1$	−7.645	*+0.003*	−7.648	*+0.051*	−7.597
$4a_1$	−5.532	*−0.286*	−5.246	*+0.053*	−5.193
1e	−5.530	*−0.287*	−5.243	*+0.053*	−5.190
$5a_1$	−1.312	*−0.013*	−1.299	*+0.002*	−1.297
$6a_1$	−0.880	*−0.008*	−0.872	*+0.037*	−0.835
2e	−0.586	*−0.007*	−0.579	*+0.024*	−0.555
$7a_1$	−0.471	*−0.010*	−0.461	*−0.020*	−0.481
3e	−0.352	*−0.008*	−0.344	*−0.035*	−0.379
Virtual orbital	+0.278	*+0.007*	+0.285	*−0.015*	+0.293
Binding[b] ($E_{\text{mol}} - \Sigma E_{\text{atoms}}$)	−0.706		−0.758		−0.932

[a] Note that there are 13 filled orbitals in H_3PO corresponding to 5 pairs of phosphorus inner-shell electrons, 1 pair of oxygen inner-shell electrons, and 7 pairs of electrons in the valence shell. The e orbitals come in pairs having identical energies so that the value of only one of the pair is given in this table. [b] The binding energy is calculated using the same basis set for the molecule as for the atoms. Since the d orbitals of the ground-state atom are not occupied, the energy for the phosphorus atom in the 731 basis is identical with that in the 73 basis.

values of these quantities for phosphine oxide. The resulting geometry selected for OPH_3 corresponds to P-H = 1.42 Å, P-O = 1.48 Å, and ∠HPH = 97°.

Results and Interpretation

Plots showing the variation of the total energy with change in the value of the phosphorus d-orbital exponent are presented in Figure 2 for phosphine oxide and for phosphine, both with a 731 basis set for the phosphorus, using the fixed s and p exponents of Table I. The resulting molecule-optimized d-orbital Gaussian exponents were found to be 0.28 for phosphine oxide and 0.33 for phosphine, corresponding, respectively, to mean d-orbital radii of 1.28 and 1.18 Å. The small differences in radius between the s, p, and d orbitals of the valence shell for phosphine oxide are shown in Figure 3. Obviously, there is no problem[2] involved in achieving good overlap of these three orbitals.

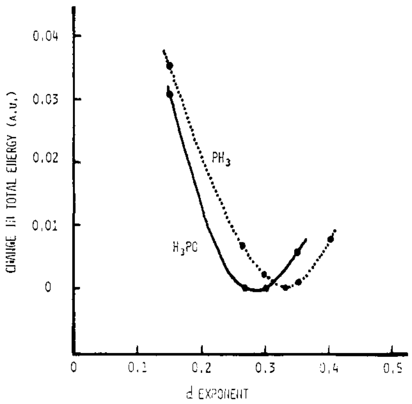

Figure 2. Optimization of the d-orbital exponent of the phosphorus in phosphine oxide (solid line) and in phosphine (dotted line), for a 731/52/2 and a 731/2 basis set, respectively. The vertical axis represents the difference in atomic units between the observed total energy and the total energy corresponding to the fully optimized d-orbital exponent.

The total electronic and all of the orbital energies as well as each calculated binding energy are shown in Table II for phosphine oxide in the following P/O/H Gaussian basis sets: 73/52/2, 74/52/2, and 731/52/2 with a d exponent of 0.30. The nuclear repulsion energy in all cases is +65.475 au and this should be added to the total electronic energy given in Table II to get the total SCF energy. It should be noted from this table that the addition of another p orbital to the 73 basis set for the phosphorus leads to a decrease in the total energy of nearly 1.7 au as compared with only 0.2 au for the addition of a d orbital. This large difference is due to the fact that the added p orbital contributes primarily to the inner shell, bolstering the three molecular orbitals (MO's)—*i.e.*, the 4a, and the pair of 1e orbitals—which are predominately attributable to the phosphorus 2p atomic orbitals (AO's). On the other hand, addition of the d orbital affects the energy of all of the MO's by about the same absolute amount.

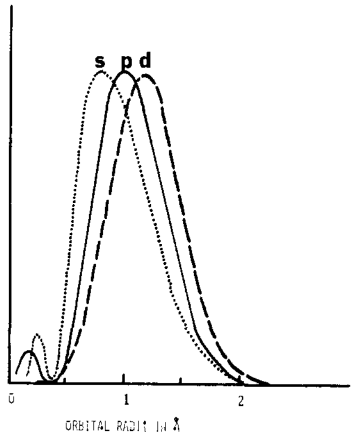

Figure 3. Radial density plot of the 3s, 3p, and 3d orbitals of phosphorus using the exponents employed in the phosphine oxide calculations (731 basis).

For all three basis sets, the calculated binding energy (exclusive of the molecular extra-correlation energy) is quite large as given in Table II; this shows that phosphine oxide is very stable with respect to dissociation into its ground-state atoms, since the omitted extra-correlation energy will also contribute toward stabili-

Table III. Detailed Population Analysis Calculations[a] for Phosphine Oxide

Orbital	P	O	H	P–O	P–H
$1a_1$	2.000[b]	−0.000	−0.000	−0.000[c]	−0.000
	2.000	*−0.000*	*−0.000*	*−0.000*	*−0.000*
	2.000	**−0.000**	**−0.000**	**−0.000**	**−0.000**
$2a_1$	−0.001	2.001	0.000	−0.002	−0.000
	−0.000	*2.000*	*−0.000*	*−0.002*	*−0.000*
	−0.004	**2.004**	**−0.000**	**−0.009**	**−0.000**
$3a_1$	2.010	−0.001	−0.003	−0.002	−0.008
	2.011	*−0.001*	*−0.003*	*−0.002*	*−0.009*
	1.999	**−0.001**	**0.003**	**−0.001**	**+0.001**
$4a_1$	2.006	−0.002	−0.001	−0.007	−0.004
	2.002	*−0.000*	*−0.001*	*−0.000*	*−0.002*
	2.012	**−0.007**	**−0.001**	**−0.025**	**−0.007**
1e[d]	4.004	−0.000	−0.003	−0.003	−0.008
	4.004	*−0.000*	*−0.001*	*−0.001*	*−0.003*
	4.013	**−0.000**	**−0.004**	**−0.001**	**−0.015**
$5a_1$	0.507	1.491	0.001	0.504	0.001
	0.503	*1.493*	*0.001*	*0.507*	*0.002*
	0.509	**1.482**	**−0.001**	**0.550**	**0.004**
$6a_1$	1.242	0.227	0.177	−0.068	0.211
	1.279	*0.223*	*0.165*	*−0.058*	*0.204*
	1.201	**0.208**	**0.197**	**0.006**	**0.219**
2e[d]	1.910	0.466	0.542	0.224	0.405
	2.033	*0.491*	*0.492*	*0.249*	*0.405*
	1.929	**0.551**	**0.507**	**0.225**	**0.417**
$7a_1$	0.466	1.384	0.050	−0.004	0.005
	0.455	*1.404*	*0.047*	*−0.004*	*−0.012*
	0.408	1.452	0.047	0.096	−0.023
3e[d]	−0.020	3.000	0.340	0.153	−0.104
	−0.029	*2.926*	*0.368*	*0.160*	*−0.115*
	+0.688	**2.631**	**0.227**	**0.533**	**−0.109**

[a] The first figure in each group corresponds to the calculation using the 73/52/2 basis set, the second (in italics) to the 74/52/2 basis set, and the third (in boldface) to the 731/52/2 basis set. [b] Mulliken gross population. [c] Mulliken overlap population. [d] Both orbitals included, so that if they were completely filled the number would be 4.0000 instead of 2.0000 electrons.

zation. The calculated stability is considerably larger than would be estimated from known bond strengths. Cottrell[16] lists 77 kcal/mol as the strength of a P–H bond and 120–130 kcal/mol for a P–O bond in the phosphoryl halides. These would give a predicted stability of 0.57 au for H_3PO compared with our computed result of 0.7–0.9 au. Since both estimates predict the system to be quite stable, we can probably conclude that calculations on this compound, which has never been prepared in spite of numerous attempts to do so, do indeed have meaning with respect to the characterization of bonding to phosphorus. Presumably the reason phosphine oxide has not yet been found is the presence of low-energy reaction-mechanism paths to decomposition products or to alternate products in the attempted syntheses.

Inspection of the array of coefficients making up the MO wave function led to the symmetry assignments (a_1 or e) of the various orbitals. By comparing the MO coefficients with the AO coefficients, the inner orbitals were readily identified. Thus, the $1a_1$ molecular orbital corresponds closely to the 1s orbital of the phosphorus atom, the $2a_1$ to the oxygen 1s, the $3a_1$ to the phosphorus 2s, and the $4a_1$ plus the two 1e orbitals to the three 2p orbitals of the phosphorus. The remaining seven filled orbitals must describe the bonding as well as the unshared electron pairs of the oxygen. Of these seven orbitals, the two pairs of 2e electrons or the two pairs of 3e exhibit the proper symmetry for encompassing P–O π character.

The results obtained from a Mulliken population analysis[17] are shown in Table III, in which the values corresponding to the 73/52/2 basis set are given in regular type, while those corresponding to the 74/52/2 set are listed next in italics and finally, the values corresponding to the 731/52/2 set are shown in boldface type. It is apparent that the population analysis from Table III agrees with the assignment previously given for the $1a_1$, $2a_1$, $3a_1$, $4a_1$, and 1e MO's. In addition, the population analysis shows that the $5a_1$ MO accounts in good part for the P–O σ bonding, the $6a_1$ and the two 2e for the P–H bonding, and the $7a_1$ and two 3e MO's for the unshared pairs of the oxygen atom. Of course, these assignments are only approximations because of the pronounced delocalization of the valence-shell orbitals.

Inspection of Table III shows that adding a p orbital to the 73 basis set (*i.e.*, going from a 73 to a 74 basis) for the phosphorus does not lead to a large change in any of the orbital populations. Except for the pair of 3e molecular orbitals, the same is true for the change upon adding a d orbital (*i.e.*, going from the 73 to the 731 basis). However, for the pair of 3e orbitals, there is a total increase of 0.71 electron associated with the phosphorus, with a concomitant reduction of 0.37 electron associated with the oxygen and a smaller decrease of 0.11 electron on each hydrogen. Likewise, the P–O overlap population attributable to the 3e orbital pair goes from 0.15 to 0.53 electron upon addition of the d orbital. The changes in overall electronic populations are also seen to be greater in the case of going from a 73 to a 731 basis set for the phosphorus than when going from 73 to 74. This gives firm evidence of the existence of p_π–d_π bonding between the oxygen and the phosphorus and is in accord with Boyd and Lipscomb's observation that the addition of a d orbital to a minimum basis set shifts charge into the bonding region.[6]

A plot of the total electron density across the plane containing the oxygen, the phosphorus, and one of the hydrogen atoms of H_3PO is shown in Figure 4. In this three-dimensional graph, the geometrical coordinates are given on the basal plane, with the electron density in this plane being plotted in the direction of the axis perpendicular to it. From Figure 4 it seems clear that the electron density around the oxygen spreads out on either side of the P–O bond somewhat behind the position of the oxygen nucleus with respect to the phosphorus. The analysis of gross electronic populations shows that the hydrogen has not gained or lost much charge on being bonded to the phosphorus but that the oxygen has gained considerable charge from the phosphorus, with both of these conclusions being in accord with standard electronegativity concepts. However, in Figure 4, it is interesting to note that the electron density in the central region of the P–H bond decreases in the direction of the phosphorus and increases in the direction of the hydrogen, so that the electrons making up the P–H bond are effectively polarized toward the hydrogen. Not surprisingly, this same effect is noticed in the case of the P–O bond, in which the total electron density at the midpoint decreases on the phosphorus side and increases on the

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(16) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958, Table 11.5.1.

(17) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

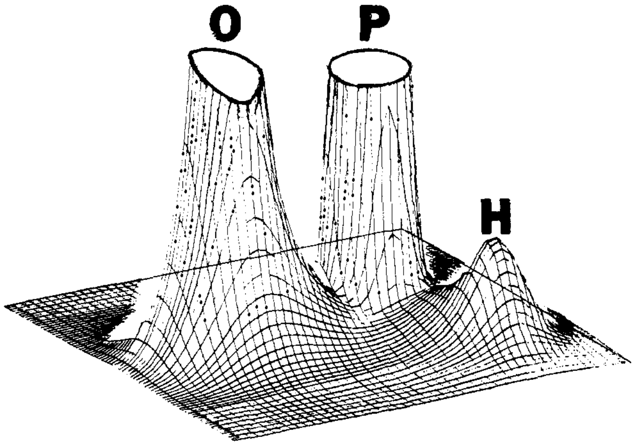

Figure 4. Total electron density across the plane containing the oxygen, phosphorus, and one of the hydrogen atoms of phosphine oxide, as described in a 731/52/2 basis. The electron density at any point in the plane is denoted by the height of the surface.

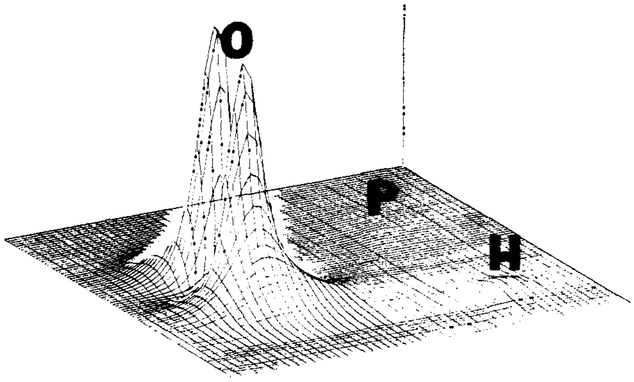

Figure 5. Electron density plot of the pair of 3e orbitals of phosphine oxide in the plane containing the oxygen, the phosphorus, and one of the hydrogen atoms. The electron density at any point in the plane is denoted by the height of the surface.

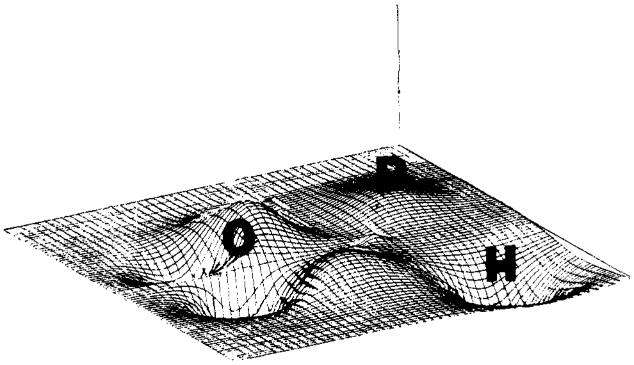

Figure 6. Electron density difference plot for the pair of 3e orbitals in the plane containing the oxygen, the phosphorus, and one of the hydrogen atoms of phosphine oxide. This plot corresponds to the difference between the 731/52/2 and the 73/52/2 basis sets, *i.e.*, to addition of a d orbital. Note that the perpendicular scale in this figure is greater by a factor of 10 than that of Figure 5.

oxygen side. This, of course, is readily reconcilable with the fact that the total gross electronic population shows the oxygen to be electronegative to the phosphorus, as expected from perusal of tabulations of averaged electronegativities.

An electron density plot is given in Figure 5 for the pair of 3e orbitals in the 731/52/2 basis set. As indicated in Table III, this pair of orbitals exhibits several tenths of an electron associated with each hydrogen atom, with the majority of the charge appearing on the oxygen. In the case where d orbitals are allowed (corresponding to the plot of Figure 5), there is also some transfer of electrons from the oxygen to the phosphorus—a transfer which shows up as a dramatic increase in the P–O overlap population. However, when one makes a plot for the 73/52/2 basis set (where d orbitals are not employed), the results look very much like the plot shown in Figure 5, except that the pair of peaks in the region of the oxygen nucleus is pushed back a relatively small distance in the direction behind the oxygen.

Although comparison of plots of the pair of 3e orbitals with and without d character is not very illuminating, a difference plot clearly shows what is happening. Such a plot is presented in Figure 6, which gives the difference in electron density between the 731/52/2 and the 73/52/2 calculations. Figure 6 clearly shows the double-lobe character of this orbital along the threefold P–O bond axis. Further, it demonstrates that when d orbitals are allowed, electrons are moved from the unshared pairs on the oxygen to a position in between phosphorus and oxygen atoms where they appear in the slice through the P–O bond given in the projections of Figure 6 as a double hump on either side of the bond axis. Similar difference plots corresponding to cuts at other angles through the P–O bond axis also show this double hump which corresponds to a p_π–d_π bond between the phosphorus and oxygen. Symmetry dictates that for any phosphoryl structure having three identical constituents (such as the three hydrogens of H_3PO), the P–C bond must be a triple bond. This is borne out by the difference plots.

It should be noted in Figure 6 that the P–O π bond is polarized in the direction of the oxygen atom. Since a total electron density plot of the kind shown in Figure 4, calculated from the wave function with d orbitals disallowed (a 73/52/2 basis set), looks very similar to the plot of Figure 4, we can conclude that the P–O σ bond is rather strongly polarized in the direction of the oxygen atom, as is the P–O π bond. By the way, since SCF orbitals are quite delocalized, the difference plot of Figure 6 shows effects other than the transfer of electrons from the oxygen lone pairs to form a P–O π bond. Thus, upon adding d character to the pair of 3e orbitals, some charge density is taken from the hydrogen and a small amount is transferred to the vicinity of the phosphorus atom, in accord with the population analysis shown in Table III.

Since the radial extent of the d orbital used in this calculation is not sufficiently broad, as demonstrated by Figure 1, and since this calculation was carried out with a rather limited basis set, it is expected that the plots of Figures 4–6 will differ somewhat from those which would result from calculations carried out with a basis set sufficiently large so as to approach closely the Hartree–Fock limit. In view of the fact that overall electron density plots are not very sensitive to a change in basis set, as long as the set is not too badly unbalanced[18] and is not absurdly small, Figure 4 should be a good representation of the truth. Figure 5

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(18) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

should also be close to the real situation; but a difference plot, such as Figure 6, is quite sensitive to the exact choice of medium-sized basis sets. However, we expect that the transfer of electrons from the oxygen lone pairs to the P–O π bond will show up clearly for any basis set, including an infinite one.

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Chemistry of Ultrasound. I. A Reconsideration of First Principles and the Applications to a Dialkyl Sulfide[1a]

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Abstract: The ultrasonic irradiation of water was effected with 280-, 610-, and 800-kHz transducers at several intensities. Conditions were varied by utilization of different initial pH, temperatures, and gaseous atmospheres in the sealed irradiation vessels. The rate of hydrogen peroxide formation was followed by titrimetric and spectrophotometric analyses. The nature of the gas and the sound intensity were established as the controlling rate factors. Irradiations of carbon tetrachloride in saturated aqueous solutions were accomplished under conditions identical with those applied to pure water. Products included carbon monoxide, carbon dioxide, hypochlorous acid, hydrochloric acid, and hexachloroethane. Product ratios were to some extent intensity dependent. Rates were likewise dependent on intensity but were unaffected by the gaseous atmospheres employed. Di-*n*-butyl sulfide (1) was subjected to the standard irradiative conditions while suspended in pure water and in saturated aqueous solutions of carbon tetrachloride. Little rate or product difference was discernible from the two media, or from the change from oxygen to argon atmosphere. The principal product under all conditions was di-*n*-butyl sulfoxide (**2**). Minor products included *n*-butylsulfonic acid (**5**), butyric acid, carbon monoxide, ethylene, acetylene, and methane. The sources of these materials were explored and a mechanistic pathway is presented which accommodates the consolidated information gathered from the irradiations of water and aqueous solutions of carbon tetrachloride and sulfide.

The irradiation of many liquids with ultrasonic waves is known to produce chemical transformations of the liquids and/or of substances dissolved in them.[2] The initiation of these reactions is somewhat speculative, but in most cases seems to be connected to the cavitation of the liquid. Cavitation bubbles, formed by phased temporary reductions of pressure at points in the liquid, are filled with vapor and dissolved gases. Reactions may take place within the cavity in the gas phase, aided by the electrically charged surface of the bubble.[3] An alternate means of initiating reactions occurs *via* high-energy intermediates which are produced from rupture of chemical bonds by the shock wave[4] or thermal gradient[5] upon collapse of these bubbles. The collapse, caused by the next compression phase, is assumed to generate local temperature rises up to 10,000°K[6a] and pressures of several tens of thousands of atmospheres.[3,6b] It is not surprising then that ionization (electron ejection)[7] and homolytic processes are detectable during irradiation.

One of the by-products of ultrasonic irradiation is a luminescence which in water has both visible and ultraviolet components.[8] This is seemingly due to cavitation bubbles with relatively high electric charges on their surfaces,[9] and the resultant electrical stresses.[10] Conflicting views[9,11] exist as to whether "sonoluminescence" is originated by chemical processes, but it is clear that in some cases[9,12,13] the quenching of luminescence by addition of small amounts of substances with high vapor pressures does *not* also quench the chemical reaction.

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(1) (a) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstracts, ORGN 18; (b) Brown University.

(2) The most extensive review of this subject is included in "Ultrasound. Physical, Chemical, and Biological Effects," E. I. El'piner, Ed., Consultants Bureau, New York, N. Y., 1964, p 371.

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