# Electronic Structure of the Phosphoryl and Thiophosphoryl Bonds[†]

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Abstract: The phosphoryl bond is presented as a resonance hybrid between singly and triply bound structures. The types of electronically excited states and a number of their potential surfaces can be understood within the confines of a singly bound model. However, a detailed analysis of the electronic distribution within the ground state shows significant contribution from the triply bound structure. In fact, increasing the electronegativity of the ligands at phosphorus increases the contribution of the triply bound structure, so that the PO bond order approaches that of a double bond. The thiophosphoryl bond may be viewed in much the same manner but is rather weaker and contains less multiple bond character than does the PO group.

As noted in a recent paper,[1] the phosphoryl group in phosphine oxide can be written in several ways,

      I   II   III
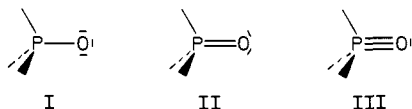
The singly bonded structure I contains only σ bonds and three lone pairs on oxygen. The d orbitals of phosphorus are not required to explain the bonding in structure I, although their energy is low enough that they may be invoked in other bonding schemes, such as II and III. These multiply bonded structures indicate the possibility of additional bonding usually ascribed to oxygen-phosphorus p_π–d_π overlap, leading to donation of the oxygen lone pairs back to the phosphorus d levels.

The customarily written structure II can be rejected as inconsistent with the threefold symmetry of the molecule. After all, *both* oxygen *e* symmetry lone pairs should participate in this back-bonding *to an equivalent extent*, leaving one a_1 oxygen lone pair. Although this symmetry requirement for triple rather than double bonding was recognized as early as 1961,[2] the incorrect resonance structure II is in nearly ubiquitous use by chemists. Recently, localized orbital calculations[3] have been used to argue for full triple bonding in phosphine oxide. Asymmetric substitution, as in XYZPO, removes the degeneracy of the oxygen lone pairs in structure I but does not prevent both from participating in back-bonding, so that even in these compounds multiple bonding would be better described by structure III than by II.

The full triple bonding implied by structure III overstates the extent of the actual π-bonding interaction. The true bonding between phosphorus and oxygen must fall somewhere between the two resonance structures I and III, and this may well be the origin of the frequent use of structure II. The aforementioned investigation[1] established that the phosphoryl bond is more closely represented by the dative structure I, with some admixture of the resonance structure III.

The evidence[1] we presented for predominantly single binding in phosphine oxide, supplemented by some additional π back-bonding may be summarized as follows. The bond formation can be thought of as an acid–base reaction in the Lewis sense, with the phosphine lone pair forming a donor bond that completes the oxygen octet. Such a dative bond gives a formally ionic Lewis structure, and indeed the Mulliken charges on P and O were found to be +0.9 and −0.7, respectively. This charge separation is mirrored in the 3.7-D dipole moment. Energy-localized SCF orbitals were found to consist of one strong σ bond and three lone pair orbitals on oxygen. These lone pairs were found by Mulliken population analysis to participate in a noticeable amount of π back-bonding to P, to the extent of some 0.2 e^- per oxygen lone

pair. It is this back-bonding which causes the phosphoryl bond length to be about the same as that in the doubly bound HPO, rather than the singly bound H_2POH. However, the primary source of PO binding is due to the σ bond. No drastic change in the localized orbitals occurs as H_3PO isomerizes to the singly bound H_2POH, except for a loss of most of the back-bonding. Finally, the PO stretching frequency in H_3PO is intermediate between those in HPO and H_2POH.

There is a great deal of experimental and theoretical evidence for the presence of multiple binding in phosphine oxides. References to experimental evidence for the occurrence of this binding have been given by Carlson and Meek[4] and Albright et al.[5] However there is much disagreement as to the magnitude of this π bonding. For example, Carlson and Meek[4] state that the bonding is best described as a "a bond possessing a character intermediate between a single and a double bond". At the opposite extreme, Wilkins et al.[6] somewhat arbitrarily obtain a PO bond order of 2.68 in trimethylphosphine oxide. References to previous ab initio theoretical calculations on phosphine oxides were given in our previous work.[1] All these calculations stress the importance of d orbitals on phosphorus in describing structure and bonding in phosphine oxides. Hudson[7] has given an extensive review of bonding in phosphoryl and other related compounds. Thermochemical data for phosphorus compounds have been compiled by Hartley et al.[8]

There is some recent experimental evidence for the interpretation of single bonding with some degree of π reinforcement. X-ray PES studies[9] show a large stabilization (3.95 eV) of the trimethylphosphine lone pair upon PO bond formation. There is a much smaller shift of the HOMO *e* symmetry oxygen lone pairs as they participate in some π back-bonding. X-ray fluorescence spectra[10] of various phosphine oxides have been interpreted as electronic transitions occurring from orbitals responsible for a weak p_π–d_π interaction.

Very recently, several workers[11,12] have suggested that p orbitals are responsible for at least part of the π-acceptor capability of

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[†]The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

phosphines. This conclusion was reached on the basis of $X\alpha$ calculations on the free phosphines[11] and PRDDO calculations on phosphine–metal complexes, using bases without d orbitals.[12] This conclusion is partially supported by our earlier finding[1] that the back-bonding in phosphine oxide is predominantly into the p orbitals of phosphine. However, our preliminary results were obtained by using a basis of only moderate quality (containing a single phosphorus d orbital). More refined calculations are clearly necessary to settle the relative importance of the phosphorus p and d orbitals in phosphine π-acceptor behavior.

In the present work we expand our investigation[1] of the phosphoryl bond in H_3PO at its equilibrium geometry in several directions. The strength of the bond and several of its dissociative potentials are presented for H_3PO in various electronic states. These ground- and excited-state surfaces are rationalized in terms of the reinforced PO single bond model presented above. Electronegative substitution at phosphorus (a sine qua non for the experimental existence of these compounds) is considered with regard to its influence on the bond strength and electronic structure of the PO moiety. For a few of the molecules we have carried out calculations in extended bases designed to probe the influence of the basis set on the back-bonding chemistry of phosphines. Finally, we briefly discuss the thiophosphoryl bond found in the phosphine sulfides.

Computational Methods

Five atomic basis sets of increasing accuracy are employed. Equilibrium geometries are found by using the minimal STO-2G* basis.[13] This is a very economical and fairly reliable means of predicting structures in phosphine oxides.[14] The split-valence 3-21G* basis[15] gives improved accuracy for energy quantities, while remaining of tractable size for correlation and some geometry calculations. The addition of a Rydberg set of s and p orbitals centered at phosphorus (with common exponent 0.039) yields a third basis set denoted 3-21G*+ that will afford better accuracy for excited states that may possess Rydberg character. The 6-31G* basis[16] is used to obtain the most accurate results for energies for all the molecules considered. The first three bases contain d orbitals only for third-row atoms (phosphorus exponent 0.55[16a] in all bases) to permit a description of the PO p_π–d_π interaction at all basis levels. The 6-31G* basis set contains polarization functions on second-row atoms as well. For the first two bases only, the 3s contaminant of the Cartesian d orbitals is excluded.

The fifth basis set, referred to as ETGC below, strives to approach the Hartree–Fock limit for the electronic density between phosphorus and oxygen as closely as is practical for these large molecules. The sp basis for phosphorus and third-row substituents is a 16s,11p even-tempered basis, generally contracted to a split-valence set 4s,3p. The phosphorus basis is supplemented by two d sets of five functions with exponents 0.22 and 0.77, since calculations with the above four bases show a large contribution from a single d function. The use of an extra set of d orbitals will of course act to *increase* back-bonding. The sp basis for oxygen and second-row substituents is a 12s,6p even-tempered basis generally contracted to the split-valence set 3s,2p. The basis for oxygen and all heavy atom substituents at P is complemented by a single set of five d functions and a diffuse s and three p functions to allow these atoms to accommodate substantial negative charge. The exponents for these diffuse functions are the appropriate even-tempered parameters α. The diffuse functions on oxygen should *reduce* back-bonding by permitting oxygen to retain a larger negative charge. The diffuse functions on the ligand atoms will *increase* PO back-bonding, by causing the phosphorus to be more positively charged due to the more negative ligand. The basis for hydrogen atoms is an unpolarized, generally contracted even-tempered basis 4s/2s, scaled by 1.2. The even-tempered portions of this basis are taken from Schmidt and Ruedenberg.[17] Second-row polarization exponents are taken from Dunning and Hay,[18] and third-row polarization

exponents are taken from Francl et al.[16a] The only exception to this prescription is F_3PO, where the large basis size forced the omission of d orbitals from the fluorines.

As the phosphine oxides are well represented within the closed shell SCF model, restricted Hartree–Fock (RHF) calculations are used to predict structures and electron distributions. The interpretation of RHF results is aided by a Mulliken population analysis[19] and by the determination of energy-localized MOs.[20] d orbital populations are taken from the 3-21G* RHF wave functions, since these exclude the 3s contaminant in the d orbitals. The most accurate total charge populations are derived from 6-31G* bases. For selected molecules, more accurate electronic distributions are obtained from the ETGC basis. As already demonstrated[1] for the phosphine oxides, the energy-localized MOs are quite different from and clearly superior to those obtained by the commonly used Boys[21] localization procedure.

Electron correlation effects are treated with two different methods. First, Møller–Plesset perturbation theory at third order[22] (MP3) is used to recover the major portion of the correlation energy of all the valence electrons at the equilibrium structures. We will use the following notation to summarize these calculations; for example, MP3/6-31G*// STO-2G* means a MP3 calculation using a 6-31G* basis at the STO-2G* RHF geometry. Because MP3 calculations with the 6-31G* basis are quite time-consuming, we often estimate energy differences by the additivity relationship

$$\Delta E(MP3/6\text{-}31G^*) =$$
$$\Delta E(RHF/6\text{-}31G^*) + [\Delta E(MP3/3\text{-}21G^*) - \Delta E(RHF/3\text{-}21G^*)]$$

that is, the correlation correction is found by using the more economical 3-21G* basis. This approximate equality is usually accurate to about 5 kcal/mol, as will be demonstrated below for a few cases (see also ref 12). Second, multiconfiguration SCF (MCSCF) calculations within the full optimized reaction space (FORS) model[23] are used to describe the dissociation of the PO bond in phosphine oxide and to characterize its excited states.

Computer codes used include ALIS,[24] for MCSCF and CI calculations and orbital localizations, and GAUSSIAN80,[25] for structure determination[26] and perturbation theory computations.

Results and Discussion

Dissociative Potentials for Phosphine Oxide. Angular momentum coupling rules require that when a ground-state phosphine oxide eliminates a closed-shell phosphine moiety, the atomic oxygen cofragment must be in a singlet state. At first glance it might appear that the removal of oxygen from phosphine oxide might be accurately described within the RHF framework, since no electron pairs are broken for this process. However, the RHF wave function dissociates to a singlet valence state of oxygen, namely $2s^2 2p_x^2 2p_y^2$, that is a linear combination of the ^1D and ^1S states of oxygen. This incorrect RHF dissociation has been noted previously.[3] Dissociation to a correct ^1D oxygen state requires the addition of the oxygen p_z orbital or, in MO language, the σ^* orbital correlating the σ dative bond, which itself becomes the phosphine lone pair upon dissociation. We have performed MCSCF calculations within the FORS model. These MCSCF calculations contain all possible configurations in which the eight reacting electrons (six from oxygen, two from phosphine) are distributed among the five active orbitals: the three oxygen lone pairs and the σ and σ^* orbitals of the oxide molecule. These calculations correctly describe the dissociation of phosphine oxide into any valence state of the oxygen atom or ion and the ground

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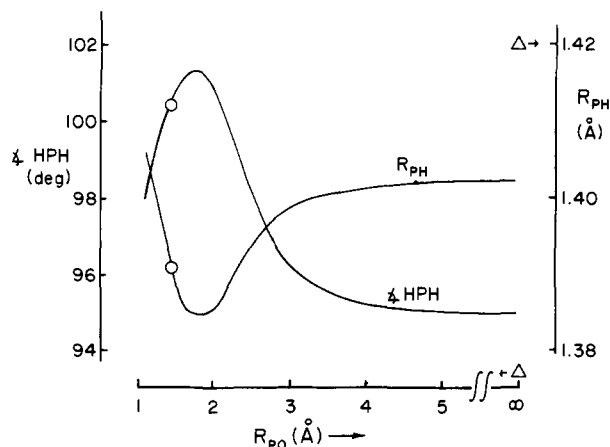(26) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214–218.

Figure 1. RHF/3-21G* geometries for phosphine oxide as a function of the PO bond length. Open circles indicate the computed equilibrium geometry of phosphine oxide, while triangles show the experimental geometry of phosphine.

state of phosphine or its positive ion.

Although the RHF function cannot correctly treat the dissociation of the ground state, this error is associated with the description of the oxygen atom, while the geometry is entirely within the phosphine group. This means it is possible to obtain valid geometries from RHF calculations, and these are shown as a function of the PO bond distance in Figure 1. It may be seen that the geometry of the phosphine group changes only slightly (7° for the HPH angle) during attachment of the oxygen. The HPH angle increases because the PO σ bond repels the PH bonds less effectively than the "wider" phosphine lone pair. This could be interpreted as favoring bonding structure I, as the hybridization at phosphorus (roughly sp^3) in this structure is much the same as for phosphine itself.

The 3-21G* geometries of the ground state during dissociation will be used for all electronic states to be considered below. Because of this, the one high-energy state which dissociates to PH_3^+ possesses a slight inaccuracy in its asymptotic geometry. This assumption also means that at finite PO distances the electronic states are not permitted to relax the internal geometry of the phosphine group. We have considered all states arising from the valence states of oxygen and ground-state phosphine and one state that dissociates to ions.

The computed MCSCF/3-21G*+ potentials for all states are shown in Figure 2. The asymptotically incorrect RHF potential for the ground state is also shown. The MCSCF PO bond strength for the ground state is 103 kcal/mol, and the MCSCF potential is 10 kcal/mol deeper than the RHF potential. The σ^* orbital in *all* excited states possesses nearly full Rydberg character at the vertical geometry. As the PO bond is stretched, this orbital acquires more and more valence character as these states approach the asymptotic valence states shown in Figure 2. MCSCF calculations, which optimize the form of this σ^* orbital, are an especially appropriate way to describe its de-Rydbergization.[27]

Each of the MCSCF wave functions for the excited states (except 2^1A_1) is dominated by a single configuration. Only the two $^1A_1$ states display much configurational mixing and then only at large PO separations. Of course, the second roots of like symmetry require a multiconfiguration computational technique such as MCSCF, even if little mixing occurs. The computed MCSCF vertical excitation energies of H_3PO are as follows: ^3E, 6.3 eV; 1^1E, 6.7 eV; $^3A_1$, 9.1 eV; 2^1A_1, 9.7 eV; $^3A_2$, 14.9 eV; and 2^1E, 16.8 eV.

The 1^1E and 2^1A_1 states are of particular interest since these states are one-electron, electric-dipole-allowed transitions from the ground state. The 1^1E state is reached by removing one of the electrons from the oxygen e shell lone pairs (which are responsible for the weak p_π–d_π interaction) and placing it in a

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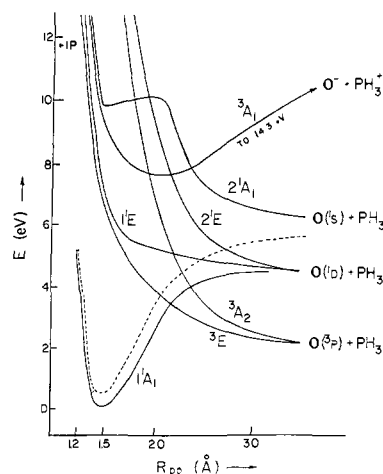

Figure 2. MCSCF/3-21G* potential energy surfaces for the dissociation of phosphine oxide. The RHF potential for the ground state is shown as a dashed curve. The MCSCF calculations contain the following numbers of configuration-state functions: $^1A_1$, seven CSFs; ^1E, four CSFs; ^3E, three CSFs; $^3A_2$, one CSF; and $^3A_1$, three CSFs.

Rydberg orbital. The steep gradient of the potential energy surface for this state then causes immediate dissociation of the oxygen atom. The orbital de-Rydbergization in the ^1E state occurs in the vicinity of the bend in this state's potential. This pattern of excitation followed by fragmentation accompanied by a transformation in the upper orbital from Rydberg to valence character is a common feature of the photochemistry of saturated molecules.[28] In contrast, unsaturated molecules typically possess valence vertical excited states which rearrange their geometry without decomposition.[29] Hence, the transition responsible for the 1^1E state is best described as n → Rydberg, an interpretation that is much more consistent with the bonding scheme I shown above than with the unsaturation implied by structure III. Identical comments apply to the ^3E state.

If more energy is available, it is possible to excite one of the electrons in the σ-donor bond to a Rydberg orbital. This transition gives rise to the 2^1A_1 state, which would dissociate to ions but for an avoided crossing. This produces the potential bump and long-range dissociative behavior (see Figure 2). No such low-lying neutral channel is available to the corresponding triplet state, which as a consequence has a bound potential leading to the indicated ions.

The other two states represent double excitations into the Rydberg orbital and are only shown for completeness at the dissociative limit. The computed vertical excitation energies place both of these states well into the ionization continuum.

Other Excited States. It is worth considering at this point the possible omissions in the MCSCF potentials just presented. The orbital space chosen for these MCSCF calculations includes only a single possible upper orbital, a Rydberg orbital of a_1 (σ) symmetry. This means that excited states produced by excitation into the e symmetry or higher a_1 Rydberg orbitals are missing in Figure 2. If such additional configurations were included, there would be numerous additional singly excited Rydberg levels lying below the doubly excited states shown in Figure 2. However, the excitations from the oxygen lone pair or the PO bond orbitals (the ^1E and 2^1A_1 states) into the lowest σ Rydberg level should be little affected by the inclusion of these states.

A small CI calculation containing only the Hartree–Fock and all singly excited configurations, with the 3-21G* basis, is an economical means of surveying the entire singlet spectrum of phosphine oxide. (The orbitals used for this calculation were taken

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from the cation so that the valence character of the lowest virtual orbitals would be greater than in the virtual set of the neutral molecule.) The first excited state is the 1^1E state already considered above, namely the dissociative n → Rydberg a_1, at 7.40 eV. The next state, at 7.80 eV, is also ^1E and corresponds to exciting an electron from the same "nonbonding" oxygen lone pair 3e orbital into the second a_1 Rydberg orbital. The next three states arise from the configuration ...$(3e)^3(4e)^1$ and lie between 8.75 and 8.85 eV. These states bear directly on the nature of the PO bond and will be addressed in greater detail below. The next two states promote the "nonbonding" electron into higher e levels, and lie at 9.87 eV ($^1A_2$) and 9.97 eV (^1E). Finally one arrives at the first states which promote an electron from the second highest MO, the PO σ bond, into the two a_1 Rydberg orbitals, producing two $^1A_1$ states at 9.97 and 10.14 eV. The first of these two is the state whose MCSCF potential (presented earlier) has the potential bump. The remaining CI states lie above the ionization potential at 11.7 eV.

The two resonance structures I and III represent the extremes of nonbonding lone pair orbitals on oxygen for I and full p_π–d_π bonding for III. If the highest occupied MO possesses π-bonding character, the lowest unoccupied e symmetry MO should be a p_π–d_π antibond. Thus orbital optimization of the three terms arising from the ...$(3e)^3(4e)^1$ configuration would reveal the nature of the upper level 4e, and thus provide additional evidence concerning the relative importance of the resonance structures I and III.

The optimization is carried out by MCSCF calculations correlating the highest four e electrons within the 3e and 4e shells. Separate optimization of the four states involved gives excitation energies of 9.06 eV (^1E), 9.12 eV ($^1A_2$), and 9.40 eV ($^1A_1$). The upper level (4e) is very similar in all states, as would be expected for different terms arising from the same electronic configuration. The population of the upper orbital in the ^1E level is almost exactly one electron. Mulliken population analysis shows a phosphorus Rydberg p population of 1.08 electrons, with a phosphorus d population of 0.004. (There are small negative populations for valence p orbitals and on the hydrogens.) The other two excited states show similar populations. Therefore, the upper level is purely Rydberg in character. (The photochemical behavior of these states may well differ from the oxygen-dissociating pathway common to most of the states where the upper orbital is of a_1 symmetry.)

HPO, HNO, and H_2CO have true π bonds containing oxygen. The lowest excitation energies[30] for these molecules are 2.3, 1.6, and 3.5 eV, respectively. In all cases the upper level of the transition can be characterized as π^*. The much larger excitation energies found for H_3PO and the complete lack of π^* character in the upper orbitals suggest less than full π bonding in the ground state.

Little experimental work has been done regarding the UV spectra of non-aryl- or non-alkenyl-substituted phosphine oxides. Hudson[7] states that "the PO bond is transparent into the far UV". A more quantitative assessment of this remark may be obtained from the trialkyl phosphine oxides. These possess blank spectra in the 200–350-nm, range,[31] which includes energies up to 6.2 eV. Both the MCSCF and CI calculations agree with this rather limited experimental data, as all vertical states of phosphine oxide are found to occur above 6 eV.

Structures of Substituted Phosphine Oxides. We have recently presented[14] the geometries of a number of monosubstituted phosphine oxides, together with a few di- and trisubstituted compounds. The substituents considered in that investigation were methyl, amino, methoxy, hydroxy, and fluoro groups. These structures were found by using the STO-2G* basis set and in a few instances the 3-21G* basis. The STO-2G* basis gives fairly good results for the geometries, except that the PO bond lengths
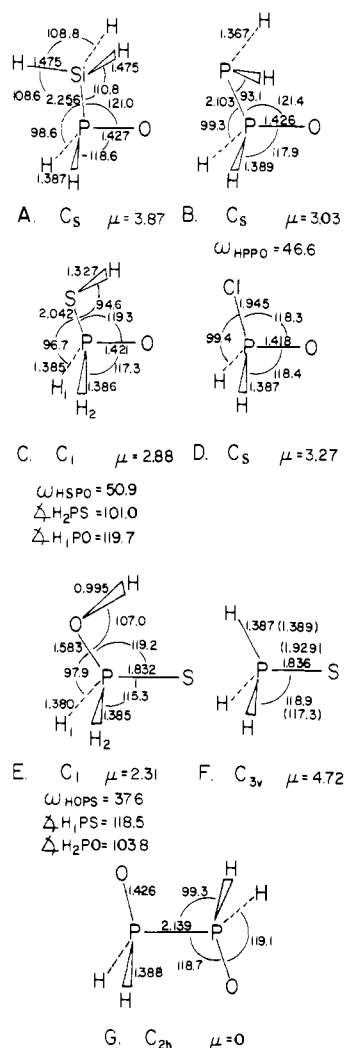
(30) G. Herzberg, "Electronic Spectra of Polyatomic Molecules"; Van Nostrand Reinhold Co.: New York, 1966.
(31) "The Sadtler Handbook of Ultraviolet Spectra"; Simons, W. W., Ed.; Sadtler Research Laboratories: Philadelphia, PA, 1979.

Figure 3. RHF/STO-2G* structures. Optimizations were constrained to the indicated point-group symmetry. Bond distances are in angstroms, and the RHF/6-31G* dipoles are in debye. The RHF/3-21G* structure for F is given in parentheses.

are shorter than experiment by about 0.03–0.05 Å. The PO bond is also calculated to be slightly shorter than experiment for the normal double bond in the XPO species, so that the errors in the STO-2G* PO bond lengths are consistent and are not related to this basis set's treatment of "hypervalence" in the PO bond. The 3-21G* basis set gives slightly longer PO bonds than experiment and requires much more computer time for geometry predictions. Thus, our previous study[14] has validated the use of the STO-2G* basis set for structure predictions, with the proviso that the PO bonds found thus will be systematically slightly too short.

We present in Figure 3A–D STO-2G* structures for the simplest monosubstituted phosphine oxides containing two third-row atoms. The substituents considered here are interesting in that, unlike the isomers formed with first-row atoms bound to phosphorus, not all will be electronegative with respect to phosphorus. The phosphino group should be electroneutral, with the silyl group actually electropositive.

Phosphinothioic acid (Figure 3C) has an alternate isomer containing a dative PS bond that is shown in Figure 3E. The simplest molecule containing such a PS bond is phosphine sulfide, whose structure is shown in Figure 3F. Diphosphine 1-oxide (Figure 3B) contains a phosphorus lone pair that can donate to a second oxygen, forming diphosphine 1,2-dioxide, whose structure is shown in Figure 3G.

The total energies of all molecules are given in Table I. For consistency in comparing results, the calculations below are performed at the RHF/STO-2G* structures, even for those cases where the 3-21G* structures are also known.[14] The only exceptions

Table I. Total Energies (in Hartrees)

molecule	3-21G*		6-31G*	
	RHF	MP3	RHF	MP3
Phosphines				
PH_3	−340.7542	−340.8790	−342.4479	−342.5715
$P(CH_3)H_2$	−379.5784	−379.7996	−381.4829	
$P(NH_2)_2H_2$	−395.4722	−395.7014	−397.4673	
$P(OH)H_2$	−415.2108	−415.4422	−417.3089	−417.6080
PFH_2	−439.1013	−439.3253	−441.3150	−441.5975
PF_2H	−537.4775	−537.8052	−540.2074	−540.6532
PF_3	−635.8784	−636.3123	−639.1214	
$P(SiH_3)H_2$	−629.3542	−629.5730	−632.5301	−632.7455
$P(PH_2)H_2$	−680.3603	−680.5986	−683.7405	
$P(SH)H_2$	−736.3567	−736.6093	−739.9680	−740.2177
$PClH_2$	−797.5056	−797.7636	−801.3624	
Phosphine Oxides				
H_3PO	−415.2070	−415.4399	−417.3067	−417.6029
$H_2(CH_3)PO$	−454.0480	−454.3753	−456.3561	
$H_2(NH_2)PO$	−469.9688	−470.3058	−472.3626	
$H_2(OH)PO$	−489.7037	−490.0442	−492.2075	−492.6791
H_2FPO	−513.5927	−513.9278	−516.2075	−516.6631
HF_2PO	−611.9920	−612.4331	−615.1192	
F_3PO	−710.3861	−710.9330	−714.0239	
$H_2(SiH_3)PO$	−703.7957	−704.1206	−707.3807	−707.7667
$H_2(PH_2)PO$	−754.8165	−755.1640	−758.6033	
$H_2(SH)PO$	−810.8182	−811.1810	−814.8347	
H_2ClPO	−871.9767	−872.3460	−876.2365	
$(OPH_2)_2$	−829.2611		−833.4567	
Phosphine Sulfides				
H_3PS	−736.3530	−736.6042	−739.9632	−740.2108
$H_2(OH)PS$	−810.8384	−811.1989	−814.8453	
Atom (in the ^1D State)				
O	−74.3088	−74.3763[a]	−84.6972	−74.8209[a]
S	−395.4980	−395.6060[a]	−397.4716	−397.5260[a]

[a] Estimated from the experimental excitation energy, as described in the text.

are unsubstituted phosphine, its oxide, and its sulfide, for which the RHF/3-21G* geometries are used.

The structures of the corresponding substituted phosphines containing either second- or third-row substituents are available on request.

Substituent Effects on the PO Bond. Since phosphorus is a relatively electropositive element, one might imagine that electronegative substitution would have a substantial effect on the PO bond. This is indeed the case, as may be seen simply by considering the computed PO bond lengths, shown in Table II. Note that trends in properties such as bond lengths, strengths, etc., will be most apparent for sequences of substituents chosen from the same row of the periodic table. It is clear that (except for methyl) increasingly electronegative substituents shorten and thus presumably strengthen the PO bond. While the magnitudes of these shortenings are quite small, the trend is unmistakably present.

The bond strengths of the PO bonds are indeed found to increase with electronegative substitution, as is also shown in Table II. These computed bond strengths are measured with respect to the dissociative product ^1D oxygen, which experimentally is 45.4 kcal/mol above the triplet ground state. The RHF bond strengths are measured relative to the correct open-shell SCF calculation on singlet oxygen rather than the singlet valence state to which the RHF functions dissociate, as described above for the unsubstituted system. Electron correlation effects on these bond strengths are incorporated by MP3 level calculations. Because it is not possible to perform an MP3 calculation on the ^1D state of oxygen, the MP3 energy of this state is estimated by adding the experimental ^3P–^1D excitation energy (45.4 kcal/mol) to the MP3 energy of ^3P oxygen. The most accurate bond strengths in Table II are those at the MP3/6-31G* level. These are estimated by using the additivity relationship described in an earlier section. In four instances the bond strengths were actually calculated to verify the accuracy of the estimation process. The calculated

Table II. Computed Phosphoryl Bond Lengths and Strengths

molecule	PO bond length[a]	PO bond strengths[b]			
		3-21G*		6-31G*	
		RHF	MP3	RHF	MP3[c]
H_3PO	1.423	90	116	101	127 (132)
$H_2(CH_3)PO$	1.417	101	125	110	135
$H_2(NH_2)PO$	1.420	118	143	124	150
$H_2(OH)PO$	1.418	116	142	126	153 (157)
H_2FPO	1.411	115	142	123	150 (154)
HF_2PO	1.410	129	158	135	164
F_3PO	1.409	125	153	129	157
$H_2(SiH_3)PO$	1.427	83	108	96	121 (126)
$H_2(PH_2)PO$	1.426	93	119	104	130
$H_2(SH)PO$	1.420	96	123	106	133
H_2ClPO	1.418	102	129	111	139

[a] STO-2G* computed bond lengths, in angstroms. [b] Energy for the dissociation of the phosphine oxide to phosphine and ^1D oxygen, in kilocalories/mole, using the indicated basis set and level of theory. [c] Estimated as described in the text, with explicitly calculated values in parentheses.

values are systematically 4–5 kcal/mol larger than the estimates based on additivity, indicating that the estimated strengths for all substituents may reliably be compared to each other.

As noted in the previous paragraph, the bond strengths in general follow the trend indicated by the bond lengths, being larger for the more electronegative substituents. However, there seems to be a limit to the ability of increasing electronegativity to increase the PO bond strength. For the series H to CH_3 to NH_2, the bond strength increases significantly but then remains nearly constant for OH and even falls off slightly for F. A similar pattern is seen for multiple electronegative substitution, where one finds an increase in the PO bond strength in going from zero to one to two fluorines, with a small decrease on adding the third fluorine atom. The third-row substituents do not reach this "electronegativity plateau", as the PO bond strength increases uniformly from SiH_3 to PH_2 to SH to Cl. Note that the PO bond strength for the electropositive silyl substituent is actually less than for unsubstituted phosphine oxide.

Experimental bond energies[32] for the phosphoryl group are about 175 kcal/mol. This is also the bond energy of the trifluoro compound,[33] the only compound for which a direct comparison is possible. The computed bond strengths are all smaller than this value. Calculational improvements such as the use of a very time-consuming triple double-ζ-plus polarization basis would likely lead to larger computed RHF bond strengths. It may be that the level of electron correlation used is also underestimating the PO bond strengths. A final source of discrepancy might be the energy assigned to the singlet oxygen. We expect, however, that our calculated bond energies should be internally consistent and certainly show which substituents produce the strongest PO bonds.

The present calculations shed only a little light on the anomalous influence of OH (or rather OR) compared to F substituents on the PO bond strength. Experimental bond strengths,[8] corrected for the excitation to singlet oxygen, are 196 kcal/mol for triethoxy- and 175 kcal/mol for trifluorophosphine oxide. However the IR stretching frequencies[8] for the triethoxy and trifluoro compounds are in reverse order, namely 1272 and 1415 cm^{-1}. Our results show that for monosubstituted compounds, OH produces slightly stronger PO bonds than does F but by a small margin of just 3 kcal/mol. On the other hand, F produces a slightly shorter PO bond than OH.

Diphosphine 1,2-dioxide (Figure 3G) possesses two phosphoryl bonds. The energy required to remove one of these oxygen atoms is 98 kcal/mol at the RHF/6-31G* level, indicating that the second PO bond is slightly weaker than the first, whose strength is 104 kcal/mol. The slightly weaker second bond is not surprising as the dioxide must accommodate two adjacent, highly positive

(32) Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper and Row: New York, 1978; pp 839–851.

(33) JANAF, "Thermochemical Tables"; Stull, D. R., Prophet, H. Eds.; U. S. Government Printing Office: Washington, DC, 1971; NSRDS–NBS37.

Table III. Phosphorus Mulliken Populations in Phosphine Oxides

	q_P		oxide[b]		
molecule	phos-phine[a]	oxide[a]	P_d	$\Delta P_d{}^c$	q_{PO}
H_3PO	0.039	0.922	0.408	0.282	0.552
			(0.713)	(0.477)	(0.640)
$H_2(CH_3)PO$	0.214	1.030	0.461	0.315	0.607
			(0.763)	(0.501)	(0.652)
$H_2(NH_2)PO$	0.354	1.071	0.497	0.328	0.606
$H_2(OH)PO$	0.468	1.182	0.532	0.330	0.594
			(0.912)	(0.557)	(0.702)
H_2FPO	0.606	1.237	0.567	0.340	0.619
			(0.847)	(0.492)	(0.814)
HF_2PO	0.985	1.481	0.666	0.347	0.634
F_3PO	1.233	1.707	0.757	0.350	0.640
			(1.194)	(0.558)	(0.711)
$H_2(SiH_3)PO$	−0.088	0.767	0.420	0.305	0.537
			(0.719)	(0.500)	(0.594)
$H_2(PH_2)PO$	0.013	0.827	0.447	0.311	0.572
$H_2(SH)PO$	0.129	0.893	0.474	0.316	0.591
H_2ClPO	0.276	0.967	0.499	0.322	0.606
			(0.871)	(0.524)	(0.763)

[a] Total 6-31G* charges on phosphorus in the phosphines and their oxides. [b] Total 3-21G* (5d) phosphorus d orbital populations for the oxides, with ETGC basis populations in parentheses. [c] Increase in the 3-21G* (5d) phosphorus d orbital populations upon oxidation of the corresponding substituted phosphine. The ETGC differences are given in parentheses. [d] 6-31G* Mulliken overlap populations for the phosphoryl bond, with the ETGC basis results in parentheses.

phosphorus atoms. This molecule possesses a threefold barrier to rotation about the P–P bond, which was probed by rigid rotation from the optimized trans structure. When the energy of the trans structure (dihedral angle = 180°) is defined as zero, a rotational maximum occurs at an eclipsed structure at 114° and 2.2 kcal/mol. There is a second minimum energy gauche structure at 65° and 1.2 kcal/mol, and the highest barrier to rotation is at the cis form (0°) with a energy of 5.5 kcal/mol. The presence of a maximum for the cis structure is due to the unfavorable alignment of the two P^+-O^- bond dipoles and the eclipsed arrangement of bonds.

Bond Orders. One expects any increase in the PO bond strength to derive from an augmented $p_\pi-d_\pi$ interaction. Hudson[7] has described various means by which substituents may affect the PO bonding. One possibility, suggested by Craig et al.,[34] is that the substituents affect the size of the phosphorus d orbital, with the more electronegative ligands causing a contraction of the d orbital, leading to more effective overlap. A recent review[35] of electrostatic calculations supports this idea. However, we find that the optimal phosphorus d exponents for H_3PO and H_2FPO are 0.523 and 0.525, respectively, by using a 3-21G* basis. Since fluorine contracts the d orbitals only minutely, all calculations described here use the standard[16a] 0.55 d exponent for phosphorus.

Most discussions of the effects of substitution on the PO bond strength assume that the back-donation from the negatively charged oxygen atom will be increased as electronegative substitution increases the positive charge at phosphorus. As is shown in Table III, the positive charge on phosphorus in both phosphines and their oxides increases as expected with electronegative substitution. It remains only to verify that this charge increase acts to increase the back-donation and thus the PO bond strength.

The simplest measure of back-donation would be to compare the phosphorus d orbital populations in the oxides to those of the phosphines. The Mulliken populations in the phosphorus d orbitals for the phosphine oxides are shown in Table III. There is a great increase in the phosphorus d population of the oxides as electronegative groups are added, but this is misleading. A similar increase occurs in the phosphines, as any lone pair on an atom

(34) (a) Craig, D. P.; Maccoll, A.; Nyholm, P. S.; Orgel, L. E.; Sutton, L. E. *J. Chem. Soc.* **1954,** 332–357. (b) Craig, D. P.; Magnussen, E. A. *J. Chem. Soc.* **1956,** 4895–4909.

(35) Kwart, H.; King, K. G. "d-Orbitals in the Chemistry of Silicon, Phosphorus, and Sulfur"; Springer-Verlap: Berlin, 1977; pp 3–5.

Table IV. Back-Bonding Populations in Phosphine Oxides H_2XPO^a

X	O[b]	P[b]	$P_s{}^c$	$P_p{}^c$	$P_d{}^c$	PO bond order[d]
SiH_3	5.385	0.604	−0.031	0.444	0.191	1.60
H	5.417	0.584	−0.017	0.431	0.170	1.58
CH_3	5.353	0.661	−0.020	0.491	0.191	1.66
Cl	5.292	0.725	−0.006	0.540	0.191	1.72
OH	5.319	0.695	0.007	0.502	0.188	1.69
F	5.275	0.741	0.042	0.507	0.192	1.74

[a] 3-21G* population analysis of the three energy-localized "lone pair" orbitals on oxygen. The substituents X are ordered by increasing PO bond length (see Table II). [b] Net Mulliken population on this atom. These may not sum to six due to trace populations on the other atoms. [c] Phosphorus net population resolved in terms of the basis function type indicated. [d] Obtained as described in the text.

bound to phosphorus will back-donate somewhat to the phosphorus d orbitals, albeit to a lesser extent than do the oxygen lone pairs in the oxides. The change in phosphorus d population upon formation of the oxide is very nearly constant. As may be seen in Table III, the *increase* in phosphorus d population upon oxidation ranges from 0.28 for phosphine to just 0.35 for trifluorophosphine, while the bond strength is increased by 30 kcal/mol (cf. Table II). The observed increases in PO bond strength are too large to be explained by the rather insignificant 0.07 e⁻ variance in the d population enlargements upon oxidation. It is also important to realize that this small differential in d population increase upon oxidation occurs in *all* the molecular orbitals, not just those involved in back-bonding. The ETGC basis, whose results will be discussed later, also shows a constant increase of 0.48–0.56 in d population upon oxidation, the larger values occurring because there are two d orbitals in this basis.

In fact, it is easier to assess the amount of back-bonding from oxygen by measuring the number of electrons given up by oxygen, rather than the number gained by phosphorus. This is readily accomplished by obtaining the energy-localized 3-21G* RHF orbitals and performing a Mulliken population analysis of the three orbitals found to be principally on the oxygen, to see to what extent these orbitals contribute electrons to phosphorus. Contour plots of these trigonally arranged "oxygen lone pair" localized orbitals in phosphine oxide have already been presented.[1] The results of a population analysis of the six electrons occupying these orbitals on oxygen are shown in Table IV. It may be seen that the π back-donation to P increases with electronegative substitution, by a noticeable amount. This trend is most apparent for the second-row substituent series CH_3, OH, F.

The bond orders shown in Table IV are assigned in the following manner: In the limit of single binding (resonance structure I), the back-bonding population on phosphorus is zero. For full triple binding (structure III), two of the four π electrons are given up to phosphorus. Adding the σ bond to the actual phosphorus π back-bonding population thus gives an *electronic* measure of the bond order. Our definition of the bond order differs fundamentally from bond orders derived empirically from observed bond distances.[36] The bond orders for various phosphine oxides shown in Table IV (1.58–1.74) indicate bonding that is closer to I(1) than to III(3) but show that resonance structure III is indeed important. The bond orders increase roughly as the computed bond strengths themselves increase with electronegative substitution.

The validity of using Mulliken populations to assign a π bond order may be tested by applying the definition to singly bound H_2POH and doubly bound HPO. The two localized oxygen lone pairs in H_2POH back-donate 0.11 electrons to phosphorus, thus giving this single PO bond a bond order of 1.11, using our definition. For HPO, the phosphorus population in the true π bond is 0.68, while the two in-plane oxygen lone pair orbitals together back-donate 0.14 electrons. The bond order predicted for this doubly bound molecule is thus 1.82, which is just larger than the

(36) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; pp 239–240. For an application to PO and PS bonds, see ref 6.

Table V. Energetics from the ETGC Basis[a]

molecule	E(phosphine)	E(oxide)	PO bond strength
H_3PO	−342.472 728	−417.371 574	108
$H_2(CH_3)PO$	−381.517 691	−456.428 000	116
$H_2(OH)PO$	−417.367 760	−492.297 914	128
H_2FPO	−441.387 240	−516.313 868	126
F_3PO	−639.217 403	−714.148 984	129
$H_2(SiH_3)PO$	−632.577 189	−707.465 636	102
H_2ClPO	−639.217 403	−714.148 984	116

[a] Total energies of the substituted phosphines and their oxides (in hartrees) and phosphoryl bond strengths (in kilocalories/mole). The ROHF energy of ^1D oxygen is −74.726 127.

1.58–1.74 range for the hypervalent phosphoryl bonds shown in Table IV. A further test of this bond order definition is afforded by our computed RHF PO stretching frequencies[1] for H_2POH (911), H_3PO (1287), and HPO (1498 cm^{-1}). The vibrational frequency of the phosphoryl bond is 64% of the way from that of a single bond to a true double bond. The bond orders presented here predict H_3PO to lie 66% of the way along the single-to-double bond scale. Electronegative substitution increases that percentage to as much as 89%. The origin of the frequent tendency among chemists to draw structure II is now apparent: the phosphoryl effective bond order approaches that of a true PO double bond with increasing electronegative substitution at phosphorus.

As shown in our previous investigation of phosphine oxide,[1] the π back-donation from oxygen occurs primarily into p orbitals on phosphorus, when using the 3-21G* basis. This remains true after substitution at phosphorus. As shown in Table IV, the p orbitals on phosphorus accept around 70% of the back-donation for all the compounds shown! The remaining 30% of the back-donation is into d orbitals and accounts for just under two-thirds of the d population increase of about 0.3 e$^-$ upon oxidation of a phosphine. (Because the p contribution to the sigma bonds by necessity decreases as these orbitals are tied up in accepting the back-bonding, d orbitals must play a larger role in the σ bonds to phosphorus. This accounts for the remaining third of the d orbital population increase upon oxidation of a phosphine.)

To determine the dependence of the foregoing analysis on basis set, we have investigated the back-bonding with the more accurate ETGC basis. Recall that the two sets of d orbitals in the ETGC basis should lead to an increase in back-bonding. The ETGC basis also contains diffuse functions on oxygen, which should serve to decrease the back-bonding, as oxygen will better be able to accommodate its negative charge. Finally the sp primitive basis is much larger than that for 3-21G*. The ETGC molecular energies are given in Table V. These energies easily surpass the lowest published RHF energies[37] for phosphine oxide and trifluorophosphine oxide. Surprisingly, the basis improvement does not substantially increase the RHF bond strengths relative to 6-31G* (compare Tables II and V).

The energy-localized orbitals for substituted molecules with this basis differ from the 3-21G* results in a number of ways. First, the d orbital populations are much increased, compared to the 3-21G* basis, as shown in Table III. The d orbital population of the trifluoro compound is nearly 1.2 e$^-$, indicative of great multiple character in the PO bond. Second, the back-bonding now occurs primarily into d rather than p orbitals. For the unsubstituted phosphine oxide, the three oxygen lone pairs donate 0.373 electrons to phosphorus. This may be resolved into the following phosphorus basis function types: s, −0.043; p, 0.119;, d, 0.298. Thus, the ETGC basis gives the result anticipated by chemists—that the back-bonding to phosphorus primarily involves its d orbitals.

To achieve this result, one must use diffuse functions on the oxygen: using two d orbitals on P without the diffuse oxygen functions leads to significantly more phosphorus p orbital involvement in back-bonding. A careful analysis of various bases

(37) Serafini, A.; Labarre, J.-F.; Veillard, A.; Vinot, G. *J. Chem. Soc., Chem. Commun.* **1971**, 996–998.

Table VI. Analysis of Basis Effects on PO Back-Bonding[a]

sp basis	no. of d on P	no. of d on O	diff sp on O	O, pop	P, pop	P_s,[c] pop	P_p,[c] pop	P_d,[c] pop
3-21G	1	0	no	5.417	0.584	−0.017	0.431	0.170
6-31G	1	1	no	5.566	0.440	−0.016	0.295	0.160
ETGC[b]	1	1	no	5.625	0.357	−0.011	0.216	0.163
ETGC[b]	1	1	yes	5.715	0.276	−0.047	0.161	0.163
ETGC[b]	2	1	yes	5.618	0.373	−0.044	0.119	0.298

[a] Mulliken population analysis of the six electrons in the localized back-bonding oxygen lone pairs. [b] Here ETGC refers to the sp basis only, without any of the supplementary basis functions indicated in the next three columns. [c] The contribution of each basis function type to the phosphorus total back-bonding population.

Table VII. Basis Effects on Phosphorus d Populations[a]

sp basis	no. of d on P	P_d pop in phosphine	P_d pop in phosphine oxide
3-21G	1	0.126	0.384
ETGC[b]	1	0.136	0.395
3-21G	2	0.233	0.683
ETGC	2	0.242	0.719

[a] Total Mulliken d orbital populations, in electrons. [b] Here this means the full ETGC basis as described in the text, except that only one phosphorus d orbital is used.

leading up to the full ETGC basis is shown in Table VI. The population in a single phosphorus d orbital is nearly unchanged as the sp basis is enlarged. However the total back-bonding to phosphorus decreases as the sp basis enlarges. The outer orbital on oxygen becomes more diffuse as the sp basis is enlarged, and this acts to decrease the back-bonding to the phosphorus p orbitals. This trend continues when deliberately diffuse functions on oxygen are added. Addition of the second d function has the expected effect of increasing the back-bonding to phosphorus, by increasing the phosphorus d population. Interestingly, the second d orbital also causes a further reduction in the role of phosphorus p orbitals. Table VI clearly shows the importance of diffuse functions at oxygen and two d orbitals at phosphorus in any attempt to reach an accurate description of the phosphoryl electronic density. Table VII shows total d orbital populations, in all molecular orbitals, for bases including one or two phosphorus d orbitals. Whether the rather small 3-21G or large ETGC sp basis is used, the phosphorus d population is dependent solely on the number of phosphorus d orbitals used.

Third, increasingly electronegative substitution changes the nature of the localized orbitals. While unsubstituted, silyl and methyl phosphine oxides still have three lone pair orbitals on oxygen and one PO σ-bonding orbital, hydroxy, fluoro, and trifluoro phosphine oxide give different results. For the hydroxy and fluoro compounds, the lone pair orbital trans to the substituent becomes so involved in back-bonding that it tips slightly toward the phosphorus, rather than slightly away from it. Once this orbital tips inward, the localization procedure leads to the formation of two banana bonds from it and the σ bond. For the trifluoro compound, two lone pairs "tip in", leading to three banana bonds. Because it is impossible to separate one bonding orbital from the three back-bonding lone pairs with the ETGC basis, it is not possible to assign bond orders as was the case for the 3-21G* basis. However, one can still look at the overall PO overlap populations, which are shown in Table III. These results show that the PO interaction increases with the ETGC basis, compared to 6-31G*, but that this increase is not enormous. Thus, the apparent change in the bonding from augmented single for H_3PO, $H_2(CH_3)PO$, and $H_2(SiH_3)PO$ to double for H_2OHPO and H_2FPO to triple for F_3PO is over-emphasized by the localization process. A plot showing the density difference between the ETGC and 3-21G* bases shows some reorganization of charge along the PO axis, as well as the expected refinements in the nuclear cusps. The differences in the total densities are thus much less than the changes in the individual localized orbital densities.

Phosphoryl and Thiophosphoryl Bonds

J. Am. Chem. Soc., Vol. 107, No. 7, 1985 1929

Table VIII. d Orbital Populations for Symmetric Molecules[a]

molecule	basis	$x^2 + y^2 - 2z^2$	xz,yz	$xy, x^2 - y^2$	total
H_3P	3-21G*	0.000	0.079	0.047	0.126
H_3PO	3-21G*	0.064	0.277	0.067	0.408
H_3P	ETGC	0.001	0.133	0.102	0.236
H_3PO	ETGC	0.079	0.516	0.118	0.713
H_3PS	3-21G*	0.036	0.169	0.066	0.271
F_3P	3-21G*	0.066	0.152	0.189	0.407
F_3PO	3-21G*	0.157	0.382	0.218	0.757
F_3P	ETGC	0.114	0.242	0.280	0.636
F_3PO	ETGC	0.243	0.623	0.328	1.194

[a] The total phosphorus d orbital populations, resolved into symmetry equivalent sets of d orbitals, in electrons.

The localized orbital scheme for assigning bond orders is a useful device for analyzing the back-bonding in the compounds considered above. However, a simpler demonstration of the presence of significant back-bonding is possible for the molecules possessing high C_{3v} symmetry. Table VIII shows the total phosphorus d orbital populations in all MOs for the all-hydrogen and all-fluorine compounds. This table shows that the increase of phosphorus d population upon oxide or sulfide formation is largely in the d_{xz} and d_{yz} "π" orbitals, that is, those orbitals which are aligned to accept the back-bonding from the oxygen p_x and p_y orbitals. The d_0 orbital which possesses "σ" symmetry and the d_{xy}, $d_{x^2-y^2}$ orbitals of "δ" symmetry gain much less population than do the π symmetry d orbitals. This result is not dependent on the particular sp basis chosen.

Thiophosphoryl Bond. Of all the group 15 dative bonds to chalconides, the PS bond is the most common after the PO bond. Indeed, one might expect these bonds to be similar in nature. The PS donor bond is much shortened by a p_π-d_π interaction, as may be seen by comparing Figure 3C, E, and F. The computed STO-2G* normal PS single bond in H_2PSH is 2.035 Å and 2.042 Å in the SH form of phosphinothioic acid. Thus the STO-2G* structures show that the donor PS bond is shortened by about 0.2 Å in phosphine sulfide and the OH form of phosphinothioic acid. Figure 3F also shows that the STO-2G* dative PS bond lengths are too short, by about 0.1 Å compared to the 3-21G* result. The same sort of error, albeit smaller, has already been noted for STO-2G* PO bonds. The 3-21G* PS bond length is probably fairly accurate, as may be seen by a comparison to measured PS bond lengths. Experimentally, the PS donor bond is 1.940 Å in trimethyl-,[6] 1.884 Å in trichloro-,[38] and 1.87 Å in trifluorophosphine sulfide.[39]

In spite of the significant contraction of the donor PS bond, this bond is much weaker than the phosphoryl bond. Typical experimental PS bond strengths,[32] corrected for the excitation to the ^1D state of sulfur, are about 106 vs. 175 kcal/mol for the PO group. As is the case for PO bonds, the computed PS bond energies are expected to be smaller than this experimental value. The computed MP3/6-31G*//3-21G* bond strength for phosphine sulfide is 71 kcal/mol, much less than the 132 kcal/mol value for the corresponding oxide.

The estimated MP3/6-31G* PS bond strength in the OH form of phosphinothioic acid is 87 kcal/mol, again much less than the 133 kcal/mol strength of the PO bond in the SH form of this compound. Thus, although it is weaker than the phosphoryl bond, the thiophosphoryl bond is also strengthened by electronegative substitution.

The 3-21G* phosphorus d population in unsubstituted phosphine sulfide is 0.271 e⁻, compared to 0.408 in the oxide and 0.126 in phosphine itself. The back-bonding population in the sulfur lone pair localized orbitals is 0.317, which is again primarily donated to p orbitals of P: s, -0.037; p, 0.264; and d, 0.089. This predominance of the p orbitals would probably not survive basis improvements of the kind considered for the oxides. The bond order of the PS bond in H_3PS is 1.32, substantially less than the

1.58 bond order in H_3PO. Thus, the role of the back-bonding interaction in the sulfides, while still significant, is rather less than for the oxides. This result is consistent with experiment. NMR studies[40] of phosphine sulfides have been interpreted as implying a smaller contribution from the π-bonding resonance structure III to the PS bond than is the case for the PO bond. It is interesting to note that d orbitals on sulfur play a very small role, as their Mulliken population in phosphine sulfide is just 0.045.

A major contributor to the weakness of the thiophosphoryl bond compared to the phosphoryl bond, beyond the diminution of the p_π-d_π bonding, is a weakening of the PS σ bond. This is borne out by the total 6-31G* Mulliken charges for phosphine sulfide (oxide): P, 0.481 (0.922); X, -0.457 (-0.719); and H, -0.008 (-0.068). Sulfur's diminished ability relative to oxygen to hold a large negative charge has decreased the charge separation in the PX bond considerably and thus weakened the formally ionic donor σ bond.

In spite of the weakness of the PS bond compared to the PO bond, the form of phosphinothioic acid containing the PS donor bond is more stable. All levels of calculation predict the sulfide to be the more stable form but with the difference decreasing with improved calculation. The final difference is small, only about 5 kcal/mol at the estimated MP3/6-31G* level. The sulfide is more stable due largely to the greater stability of the OH bond vs. the SH bond. Typical OH and SH bond energies are 110 and 87 kcal/mol, respectively,[31] offsetting the difference in the stability of the PS and PO bonds.

Finally, one may compare the hypervalent H_3PY with the normal valent H_2PYH molecules for Y = O or S. There is little difference, as MP3/6-31G* predicts the normal valent compound to be the more stable form by 3 kcal/mol for Y = O vs. 4 kcal/mol for Y = S. These gaps would of course widen if the normal valent structures were also obtained from 3-21G* calculations. In contrast, note that we have found[14] the substituted systems to favor the hypervalent forms for Y = O. This reflects the strengthened PO bond resulting from electronegative substitution.

Summary

The electronic structure of the phosphoryl bond in a wide variety of substituted phosphine oxides has been examined. The traditional representation of this bond as double has been eschewed on group theoretical grounds and is supplanted by a model involving a resonance between singly and triply bound structures. For the unsubstituted phosphine oxide, the bond order as defined with the use of electronic back-bonding populations indicates that both resonance structures are quite important. The singly bound structure is the more dominant contribution, as the bond order in phosphine oxide is found to be smaller than that in the conventionally doubly bound HPO.

A variety of substituents formed by using second- and third-row atoms were considered, particularly with regard to their influence on the phosphoryl bond. Most of the ligands are electronegative with respect to phosphorus and act to strengthen the PO bond over that in phosphine oxide. The lone electropositive substituent, the silyl group, acts to weaken the phosphoryl bond compared to phosphine oxide. Increasingly electronegative substitution at phosphorus is accompanied by shortening PO bond lengths, increasing energies for dissociation of oxygen and increasing PO bond orders. Fluorine substituents behave somewhat anomalously, as one fluorine is less effective than one hydroxy group in strengthening the PO bond and three fluorines are less effective than two.

The relative importance of the back-bonding triply bound structure is found to increase with electronegative substitution. As measured by the actual electronic back-bonding populations from oxygen to phosphorus, the phosphoryl bond orders approach but do not quite reach the PO bond orders found for doubly bound HPO. A possible explanation for this increase in back-bonding is the increasing positive charge developed on phosphorus by increasingly electronegative substituents. Our earlier surprising

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finding[1] that the P-backbonding interaction involves the phosphorus p orbitals to a greater extent than the d orbitals does not survive improvements in the atomic basis set. Although the total back-bonding populations do increase with electronegative substitution, the increase in d orbital population at phosphorus upon oxidation is found to be very nearly constant.

Multiconfiguration SCF potential energy surfaces for the dissociation of oxygen from some of the excited electronic states of phosphine oxide were presented. The majority of these states are found to be repulsive, although a small potential bump is present in one of the higher singlet levels and one triplet state has a bound potential leading to ions. The states are best described as transitions from nonbonding oxygen lone pair orbitals to a phosphorus a_1 Rydberg orbital. MCSCF optimization of the lowest vertical states, for which the upper orbital was of e (that is π) symmetry, showed that this π borbital possessed Rydberg character, rather than being a p_π–d_π antibonding orbital as implied by the triply bound resonance structure. This finding may be modified with the use of the largest basis set, and electronegative substituents at the phosphorus are likely to increase the π valence character of the excited orbital. At higher excitation energies, electrons may be excited from the PO dative σ bond into phosphorus Rydberg levels. The excited states can be rationalized entirely in terms of a singly bound resonance structure for the ground state.

Calculations on the thiophosphoryl bond show that it is weaker than the PO bond. The relative importance of the triply bound resonance structure in phosphine sulfide is less than in the oxide. Otherwise, the bonding picture largely resembles that of the phosphine oxides. Electronegative substitution acts to increase the PS bond strength, just as for the phosphoryl bond itself. d orbitals on sulfur play little role in the dative sulfide bonding.

A paper comparing the phosphoryl and thiophosphoryl bonds to valence isoelectronic molecules such as the singly bound H_3SiF and triply bound H_3SN will appear shortly.[41]

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Picosecond Studies of Ruthenium(II) and Ruthenium(III) Porphyrin Photophysics

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Abstract: We report the results of picosecond and slower time scale transient absorption and emission measurements on a series of ruthenium(II) and ruthenium(III) octaethylporphyrins ($Ru(OEP)(L_1)(L_2)$). The ruthenium(II) porphyrins are of three types. First are the carbonyl complexes in which L_1 = CO and L_2 = EtOH, pyridine (py), or 1-methylimidazole (1-MeIm), which all exhibit similar spectral and kinetic behavior. The lowest excited states of these molecules are assigned as the ring $^3T(\pi,\pi^*)$ in agreement with previous work on similar complexes. The $^3T(\pi,\pi^*)$ state has a lifetime of ~75 μs at room temperature in degassed solution, as measured by decay of phosphorescence emission at 657 nm or relaxation of absorption changes induced by a 10-ns laser flash. Absorption difference spectra obtained upon excitation with a 35-ps flash do not decay over a 6-ns time scale, in agreement with the slower measurements. The spectra exhibit bleaching in the ground-state bands and the appearance of two new transient absorption peaks (log ϵ ~3.7) near 720 and 815 nm; these features are consistent with the assignment of the transient as a metalloporphyrin (π,π^*) triplet. The $^1Q(\pi,\pi^*)$ lifetimes in these carbonyl complexes appear to be <35 ps. Different photophysical behavior is observed for $Ru^{II}(OEP)(P\text{-}n\text{-}Bu_3)_2$. We assign the lowest excited state of this complex as a $(d_\pi,e_g(\pi^*))$ metal-to-ring charge transfer (CT) state. The lifetime of this transient is 12 ± 3 ns, as measured by decay of the absorption changes in toluene following picosecond excitation. The absorption difference spectrum contains a distinct new absorption peak near 710 nm, which is expected for a (d,π^*) CT excited state on the basis of resemblances with ground-state spectra of metalloporphyrin π-anion radicals. The absorption changes observed upon excitation of $Ru^{II}(OEP)(NO)(OMe)$ in toluene with a 35-ps flash decay in two steps, with lifetimes of ≤50 ps and >5 ns. These components are tentatively assigned to relaxation of the ring $^1Q(\pi,\pi^*)$ and $^3T(\pi,\pi^*)$ excited states. The triplet decay may proceed via ring $(\pi) \rightarrow [\text{metal } d_\pi + NO(\pi^*)]$ CT states predicted to be in the proper energy range from previous theoretical work. Finally, excited Ru^{III}-$(OEP)(P\text{-}n\text{-}Bu_3)(Br)$ decays completely in ≤35 ps, possibly via a (π,d_π) ring-to-metal CT excited state. Our results are discussed in terms of recent absorption and emission measurements and calculations on d^6 metalloporphyrins and are compared to previous picosecond measurements on analogous osmium(II) porphyrins.

Recent absorption and emission studies and iterative extended Hückel (IEH) calculations have been performed on a number of Fe^{II}, Ru^{II}, and Os^{II} porphyrins.[1,2] These investigations have shown that the electronic properties of these complexes are strongly affected by the σ-donating and π-accepting nature of axial ligands. The relative energies of the lowest ring (π,π^*) and metal-to-ring $(d_\pi,e_g(\pi^*))$ charge-transfer (CT) excited states appear to be of major importance in governing the photophysical behavior. A

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