Heteroatom Chemistry
Volume 11, Number 1, 2000

An Ab Initio Study of the Comparative Stabilities of the Simple Phosphine Oxide Tautomers

D. B. Chesnut

P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

Received 13 August 1999

ABSTRACT: *High level ab initio quantum mechanical model chemistries have been used to study the relative stabilities of the simple phosphine oxides tautomers OPH_3/PH_2OH and $OPH(OH)_2/P(OH)_3$ and related molecules. It is found that the two PH_2OH isomers are virtually equi-energetic and only slightly more stable than OPH_3 itself, and the oxides with one or more hydroxyl groups are significantly more stable than their hydroxide tautomers. The difference in stability arises mainly from the variation of the $P{=}O$ bond energy among the various species, the $P{=}O$ bond energy increasing with the number of hydroxyl groups present. The effects of solvation in aqueous solution are estimated by reaction field polarized continuum models and by explicit calculations of OPH_3 and PH_2OH hydrogen bound to a single water molecule. Both approaches indicate that the oxide form is significantly stabilized by its aqueous environment.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:73–80, 2000

INTRODUCTION

A central tenet of organophosphorus chemistry is that in systems like phosphorous acid, $P(OH)_3$, and phosphonic acid, $OPH(OH)_2$, the latter species is the highly dominant form because of the greater strength of the $P{=}O$ bond relative to a P–O single bond [1]. Guthrie [2] has estimated the thermodynamics of such reactions in aqueous solution and calculates a change in the Gibbs free energy, ΔG, of -14.1 kcal/mol for the reaction

$$P(OH)_3 \rightarrow OPH(OH)_2,$$

providing strong support for this notion. On the other hand, Schmidt et al. [3] and Nguyen and Hegarty [4] both have theoretically compared the relative energies of OPH_3 and $HOPH_2$ and found the latter to be 5.7 and 5.0 kcal/mol lower in energy, respectively. But although both these studies employed rather advanced approaches (MP3/6-31G(d) [3] and MP4SDQ/6-31G(d,p) [4]), both used structures optimized at the 3-21G(d) level, and the basis set used by Nguyen and Hegarty for phosphorus [3-21G(d)] is likely inadequate. More powerful approaches to energy calculations are currently available, and it is worthwhile to reexamine the energies of these and other oxides and hydroxides of phosphorus as we do in this article.

The simplest phosphine oxide, OPH_3, has been of great theoretical interest in the past few years as researchers try to determine the proper view of bonding in this unusual compound [3–14]. To date, it has only been observed in an argon matrix at very low temperatures in the detailed FTIR study by Withnall and Andrews [15] of photolysis products of the PH_3-O_3 complex formed by reagent codeposition with excess argon at 12–18 K. Phosphine oxide, OPH_3, and its *syn*- and *anti*-phosphinous acid tautomers, PH_2OH, were the primary products, along with phosphonic acid, $OPH(OH)_2$, and HPO. The two isomers of PH_2OH were not interconverted by additional irradiation. However, further irradiation did

CCC 1042-7163/00/010073-08

cause HPO to disappear and to be replaced by the HOOPO and $HP(O_2)O$ isomers; photoisomerization of $HP(O_2)O$ yielded metaphosphoric acid, $HOPO_2$. All the species were identified by isotopic substitution and mechanistic considerations as well as knowledge of OH, PO, and P = O vibrational frequencies of related species. No discussion was given regarding a quantitative measure of the relative amounts of the various species.

The fact that phosphonic acid but not phosphorous acid was observed is consistent with the previously stated ideas regarding these two molecules. However, the fact that both isomers of PH_2OH coexisted with OPH_3 indicates that all these tautomeric molecules might be of relative equal thermodynamic stability. The purpose of this article is to investigate the energetics and thermodynamics of these four species and related molecules using relatively high-level, accurate quantum mechanical techniques. As we shall show, phosphonic acid is considerably more stable than phosphorous acid, while the *syn*- and *anti*-PH_2OH tautomers are virtually equi-energetic and only slightly more stable than OPH_3 itself. The difference in stability arises mainly from the variation in strength of the P = O bond among the simple oxides.

THEORETICAL METHODS

Calculations were performed using the G3 [16], G3MP2 [17], and CBS-Q [18] model chemistries and a simple density functional approach that employed the B3LYP [19–21] model. The G3, G3MP2, and CBS-Q approaches are compound methods involving a variety of basis sets and advanced theoretical corrections to provide good energy estimates for what would otherwise be impractical single-point calculations. The G3 and G3MP2 methods are effectively at the QCISD(T) level with a prescribed large basis set and provide absolute average deviations for heats of formation of a large set of test molecules of 0.94 and 1.18 kcal/mol, respectively. The CBS-Q approach performs a basis set extrapolation in order to minimize basis set truncation error, in which successively smaller basis sets are employed to provide corrections at higher levels of theory. An average absolute deviation from experiment of 1.0 kcal/mol is reported for heats of formation. All these approaches calculate scaled zero-point energies (ZPE) and frequencies at the Hartree-Fock 6-31G(d) level. In all cases, the thermal corrections to the energy, enthalpy, and Gibbs free energy employ the standard expressions for the ideal gas in the canonical ensemble. In our current application of the G3 and G3MP2 methods, which are not currently programmed into the Gaussian 98 code [22], we used the ZPE and thermal corrections for both the enthalpy and Gibbs free energy from G2MP2 [23] calculations that take the same approach for these quantities as do the G3 methods.

The simple density functional (dft) method employed here (B3LYP) calculated equilibrium geometries and vibrational frequencies at the B3LYP/6-31 + G(d,p) level and energies at the B3LYP/6-311 + + G(3df,2p) level. Thermal corrections to the high-level energy were taken from the B3LYP/6-31 + G(d,p) calculations, and no scaling of the ZPE or vibrational frequencies was made in this approach. We estimate that this dft model should be accurate to about 2–3 kcal/mol.

All our calculations were performed using the Gaussian 98 code [22] with the exception of the AIM studies [24–26] where Gaussian 94 [27] was required due to problems in Gaussian 98 with this particular application.

RESULTS AND DISCUSSION

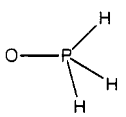
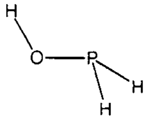
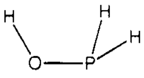
Molecular Structures

As previously indicated, the structures employed in the model chemistries were typically of the MP2/6-31G(d) type [the 6-31 + G(d,p) basis was used in the B3LYP studies]. The (scaled) calculated frequencies at the RHF/6-31G(d) level agree well with those observed [15], showing mean absolute deviations of 12 cm^{-1}, 21 cm^{-1}, and 20 cm^{-1} for the OPH_3, *syn*-PH_2OH, and $OPH(OH)_2$ species, respectively. The good agreement of calculated and observed frequencies for the $OPH(OH)_2$ molecule is confirmation of our theoretically optimized structure. Only a few frequencies for *anti*-PH_2OH were noted, and they also agreed well with theory.

Because it has served as a testing ground for the understanding of bonding in the phosphine oxides, the structural parameters for OPH_3 (and PH_2OH) were also determined at the QCISD/6-311 + + G(2d,p) level and are given in Tables 1 and 2 along with those obtained at the MP2/6-31 + G(d,p) level; the QCISD results are likely theoretically rather accurate.

The structures of the phosphine oxides and hydroxides studied here are of some interest. All the structures are basically tetrahedral about phosphorus as shown in Scheme 1, which schematically illustrates the structures in the progression from phosphoric acid (**1**) to phosphinous acid (**6**). Phosphoric acid (**1**) was constrained to have a three-fold axis and ends up with C_3 symmetry (not C_{3v}) with the oxygen hydrogens in an “up” or *syn* arrangement with respect to the multiply bound oxygen. The

TABLE 1 Structural Parameters (Å and degrees) for Phosphine Oxide and its Phosphinous Acid Tautomers in the QCISD/6-311+ +G(2d.p) and MP2/6-31+G(d.p) Approaches[a]

	 *OPH_3*	 *anti-PH_2OH*	 *syn-PH_2OH*
OP	1.4807 (1.5039)	1.6716 (11.6921)	1.6630 (1.6821)
PH	1.4026 (1.4018)	1.4118 (1.4069)	1.4173 (1.4138)
OH	–	0.9614 (0.9650)	0.9621 (0.9660)
HPO	116.76° (117.01°)	98.11° (97.96°)	100.78° (100.71°)
HOP	–	109.25° (109.41°)	114.04° (114.72°)
HPH	101.30° (100.98°)	93.12° (93.96°)	92.62° (93.25°)
∠HPOH[b]	–	132.82° (132.42°)	47.40° (47.71°)

[a]The MP2 results are given in parentheses.

[b]∠HPOH is a dihedral angle.

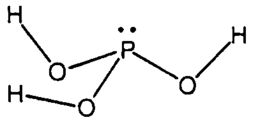
TABLE 2 Energy Data for OPH_3, and *anti*- and *syn*-PH_2OH[a]

	OPH_3	*anti-PH_2OH*	*syn-PH_2OH*
G3	−418.21240	−418.21268	−418.21232
	0.03074	0.03062	0.03064
G3MP2	−417.88405	−417.88435	−417.88394
	0.03074	0.03062	0.03064
CBS-Q	−417.87260	−417.87073	−417.87061
	0.03159	0.03149	0.03153
B3LYP	−418.44782	−418.44849	−418.44819
	0.03089	0.03126	0.03115

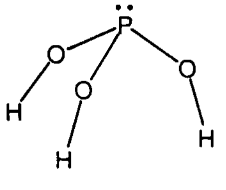
[a]Ground state electronic energies and zero-point energies (hartrees) for the various model chemistries. There are no empirical corrections in the B3LYP model.

HOP=O dihedral angle (at the MP2/6-31+G(d,p) level) is 35.7°. Removal of the multiply bound oxygen (to yield phosphorous acid, **2**) leaves the shape of remainder of the molecule virtually unchanged with an effective dihedral angle of 36.2°; Scheme 1 shows that the remaining three-fold axis in **2** coincides with the direction of the phosphorus lone pair.

The determination of the equilibrium structure of phosphorous acid is an interesting case study in optimization and shows that great care need be taken in identifying structural stationary points as minima or saddle points. Although starting the phosphoric acid optimization in a "down" or *anti* conformation of the hydrogens returns the molecule to the stable *syn* form, such is not the case for phosphorous acid whose *syn* (**2**) and *anti* (**7**) conformers are shown below. The structure **7** is a stationary point on the potential energy surface. However, in contrast to **2**, which is a true minimum (no imaginary frequencies), **7** corresponds to a second-order saddle point (a second-order transition state) and exhibits two imaginary frequencies (of two-fold degenerate *E* symmetry). What was initially disconcerting was that, at the MP2/6-31+G(d,p) level, **7** has an energy some 1.04 kcal/mol lower than **2**. However, at the MP2/6-311+ +G(3df,2p)//MP2/6-31+G(d,p) level **2** is lower than **7** by 0.95 kcal/mol.

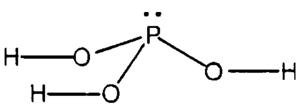


2



7

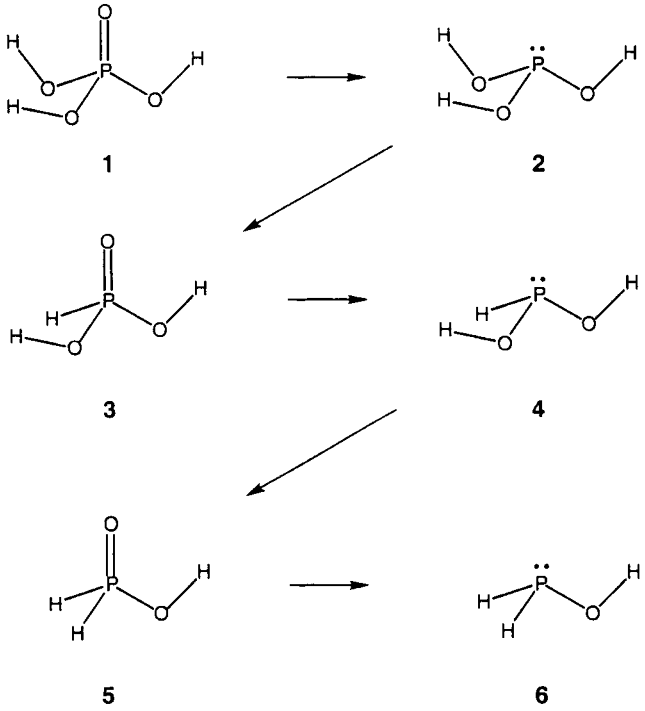
Using the synchronous transit-guided QST2 method of Peng and coworkers [28], another transition state (**8**) is found between **2** and **7** with an intermediate dihedral angle of 85.0° and an energy 4.27 kcal/mol above **2** at the MP2/6-311+ +G(3df,2p)//MP2/6-31+G(d,p) level. The transition state **8** has three imaginary frequencies (*A* and *E* symmetries), a third-order saddle point. Similar results concerning energies and structures are obtained at the B3LYP/6-311+ +G(3df,2p)//B3LYP/6-31+G(d,p) level.



8

Energetics

OPH_3 and $OPH(OH)_2$ and their tautomers were treated in some detail as presented in Tables 2–5 where ground state energies, reaction enthalpies, and Gibbs free energies are tabulated by four different theoretical approaches. The results of the various approaches are basically consistent and well within their stated error limits. OPH_3 and the *syn*- and *anti*-isomers of PH_2OH are basically equi-energetic, with the PH_2OH species being slightly preferred in terms of the calculated Gibbs free energy changes; these results are entirely consistent with those of Withnall and Andrews [15]. Tables 4–5 shows that the $OPH(OH)_2$ species is much stabler than its $P(OH)_3$ tautomer, again in good agreement with the FTIR study [15] and with the energy estimations of Guthrie [2], who calculates a Gibbs free energy change of −14.1 kcal/mol in aqueous solution. Guthrie's result and our own calculations are about what one would



SCHEME 1

TABLE 3 Enthalpy and Gibbs Free Energy Changes (kcal/mol) for the Various Model Chemistries ($OPH_3 \rightarrow$ anti-$PH_2OH \rightarrow$ syn-PH_2OH)

Δ*H*	G3	0.06	0.14
	G3MP2	0.04	0.17
	CBS-Q	1.41	-0.01
	B3LYP	0.12	0.02
	$\bar{x}$	0.41 ± 0.58	0.08 ± .08
Δ*G*	G3	-1.19	0.34
	G3MP2	-1.21	0.38
	CBS-Q	0.17	0.21
	B3LYP	-1.14	0.23
	$\bar{x}$	-0.84 ± 0.59	0.29 ± 0.07

TABLE 4 Energy Data for $P(OH)_3$ and $OPH(OH)_2$[a]

	$P(OH)_3$	$OPH(OH)_2$
G3	-568.68786	-568.70989
	0.04137	0.04190
G3MP2	-568.27544	-568.29647
	0.04137	0.04190
CBS-Q	-568.25991	-568.28306
	0.04243	0.04325
B3LYP	-569.03530	-569.05421
	0.04217	0.04298

[a] Ground state electronic energies and zero-point energies (hartrees) for the various model chemistries. There are no empirical corrections in the B3LYP model.

TABLE 5 Enthalpy and Gibbs Free Energy Changes (kcal/mol) for the Various Model Chemistries ($P(OH)_3 \rightarrow OPH(OH)_2$)

Δ*H*	G3	-13.86
	G3MP2	-13.24
	CBS-Q	-14.46
	B3LYP	-11.93
	$\bar{x}$	-13.37 ± 0.94
Δ*G*	G3	-14.20
	G3MP2	-13.57
	CBS-Q	-14.36
	B3LYP	-11.31
	$\bar{x}$	-13.36 ± 1.22

expect on the basis of mean bond energies [29]. We need to remember that at this point we have calculated gas-phase species, and the work of Guthrie and of Withnall and Andrews is for other phases, aqueous solution in the former case and a cold argon matrix in the latter. We estimate effects of hydration later. The neutral material matrix work is likely well modeled by the gas-phase calculations, and the effects of polarization and hydrogen bonding in water can be and often are significant. We note in passing that the relative stability of phosphonic acid over phosphorous acid does not appear to be the case for the sulfur analogs, for which Keck et al. [30] find experimental evidence from mass spectroscopy studies that $P(SH)_3$ is stabler than $SPH(SH)_2$.

The leading cause of the difference in stability between the OPH_3/PH_2OH and $OPH(OH)_2/P(OH)_3$ cases lies mainly in the relative strength of the P=O bond. Table 6 contains G3MP2 and G2MP2 data for the reaction heats of the various steps in converting the oxides to their corresponding hydroxy tautomers, including the $OPH_2(OH) \rightarrow PH(OH)_2$ reaction. The P=O bond in OPH_3 is noticeably weaker than those of the other molecules studied, and one sees a steady progression in bond strength as hydroxyl groups are added. Although there is a somewhat compensating increase in the P-OH bond energy as the number of hydroxide groups is increased, it is the change in the P=O bond energy that is dominating.

Bonding Analysis

Bader's atoms-in-molecules (AIM) approach [24,25] is a very useful theoretical interpretation of the quantum mechanical electron density. In the AIM approach, molecular subsystems are defined in terms of the vector field of the gradient of the electron density, $\nabla\rho$. Zero flux surfaces ($\vec{n}\nabla\rho = 0$, where $\vec{n}$ is the unit vector normal to the surface) enclose the subsystems. Each particular gradient path starts and ends at what are called critical points, and nuclei act as attractors for gradient paths within each subsystem. The region of three-dimensional space traversed by all gradient paths that terminate at a given attractor defines the basin of the attractor; each attractor and its associated basin are called "atoms".

The contribution to the electron number from the occupied orbital $|i\rangle$ in the basin Ω_A is given by

$$\langle i|i\rangle_A = \int_{\Omega_A} \langle i|i\rangle d\bar{r} \tag{1}$$

In the Hartree-Fock approach (which we employ here in the AIM studies), the charge $q(A)$ associated with a nuclear attractor in the A basin is given by summing over all the orbital contributions $\langle i|i\rangle_A$ and subtracting from the associated nuclear charge.

$$q(A) = Z_A - \sum_i \langle i|i\rangle_A \tag{2}$$

Following Bader's approach, Cioslowski and Mixon [26] have defined a natural bond order in the atoms-in-molecules picture using a localization procedure by Cioslowski [31,32] based on the idea of atomic overlap matrices. They show that the total number of electrons in the molecule may be naturally partitioned as

$$\begin{aligned} N &= \sum_i \sum_A \langle i|i\rangle_A^2 + 2\sum_i \sum_{A<B} \langle i|i\rangle_A \langle i|i\rangle_B \\ &= N_{\text{atomic}} + N_{\text{diatomic}} \end{aligned} \tag{3}$$

so that the covalent bond order, $p(AB)$, between atoms A and B is given by

$$p(AB) = 2\sum_i \langle i|i\rangle_A \langle i|i\rangle_B \tag{4}$$

The localized orbitals $|i\rangle$ are found by maximizing the atomic contribution, N_{atomic}, while maintaining the first-order density matrix constant. These bond orders relate well to conventional ideas of single and multiple covalent bonds.

TABLE 6 G3MP2 and G2MP2 Enthalpy Changes (kcal/mol) for the Interconversion of the Phosphine Oxides to their Hydroxide Tautomers[a]

	ΔH	
Reactions	*G3MP2*	*G2MP2*
OPH_3 = O + PH_3	108.04	110.11
PH_3 = ·H + ·PH_2	79.07	82.23
·H + O = ·OH	−101.45	−100.92
·OH + ·PH_2 = *anti*-$HOPH_2$	−85.63	−90.58
	0.03	0.84
$OPH_2(OH)$ = O + PH_2OH	130.49	131.82
PH_2OH = ·H + ·HPOH	75.40	76.97
·H + O = ·OH	−101.45	−100.92
·OH + ·HPOH = $HP(OH)_2$	−96.27	−99.28
	8.17	8.59
$OPH(OH)_2$ = O + $HP(OH)_2$	142.10	142.83
$HP(OH)_2$ = ·H + ·$P(OH)_2$	73.50	77.16
·H + O = ·OH	−101.45	−100.92
·OH + ·$P(OH)_2$ = $P(OH)_3$	−100.92	−105.72
	13.23	13.35
$OP(OH)_3$ = O + $P(OH)_3$	143.61	143.99

[a] The radicals are in doublet states while oxygen is taken to be in its ^3P state. The PO bond dissociation reaction for $OP(OH)_3$ is included for completeness.

Table 7 shows geometrical and AIM parameters for the multiple PO bond in the phosphine oxides studied here, in which the AIM calculations have been carried out at the RHF/6−31+G(d,p)//MP2/6−31+G(d,p) level. The molecules are listed in that table in ascending order of the multiple PO bond energy as revealed in Table 6. We note that, as expected, the equilibrium bond distance shortens and the electron density at the PO bond critical point, ρ_{bcp}, increases as the stability of the bond increases with increasing number of hydroxyl groups. This latter relationship between bond distance and density at the bond critical point is that generally observed in the AIM approach [33]. The Laplacian at the bond critical point, $(\nabla^2\rho)_{\text{bcp}}$, is positive, indicative of removal of charge from the internuclear region and, thus, of ionic character of the bond. The highly ionic nature of the multiple PO bond is well known and is further reflected by the large negative charge on oxygen and the very large positive charge on phosphorus.

There are three primary observations to be made with respect to the data in Table 7; it pertains to the increasing stability of the PO bond as the number of hydroxyl groups on the molecule is increased. First, the ionic character of the bond is clearly increasing as witnessed by the increasing positive charge on phosphorus. Second, this increase in positive charge on phosphorus does not come from donation to the oxide oxygen, but rather to the other portion of the molecule. Finally, we note that the covalent bond order, $p(PO)$ actually decreases as the bond stability

TABLE 7 Geometrical and AIM Parameters for the PO Multiple Bond in the Various Oxides[a]

	R	*p(PO)*	*q(O)*	*q(P)*	ρ_{bcp}	$(\nabla^2\rho)_{bcp}$
OPH_3	1.5039	0.805	−1.58	+3.51	0.219	+1.48
$OPH_2(OH)$	1.4948	0.759	−1.59	+3.68	0.224	+1.58
$OPH(OH)_2$	1.4891	0.724	−1.60	+3.83	0.229	+1.64
$OP(OH)_3$	1.4872	0.693	−1.61	+3.97	0.232	+1.64

[a] The parameters correspond to the PO bond distance (*R*, in Å at the MP2/6-31+G(d,p) level), the covalent bond order, *p*(PO), the charge on oxygen (*q*(O)) and phosphorus (*q*(P)), and the election density (ρ_{bcp}) and Laplacian ($(\nabla^2\rho)_{\text{bcp}}$) at the bond critical point (bcp).

increases. Clearly, as the ionic nature of the PO bond increases, its covalent character will tend to decrease. We conclude from this that the ionic bonding in the multiple PO bond is dominant in these molecules and that the removal of charge from phosphorus by the nonoxide portion of the molecule increases the ionic character and overall strength of the PO bond.

Effects of Solvation

The data of Guthrie [2] regarding the relative stabilization of $P(OH)_3$ and $OPH(OH)_2$ was for aqueous solution whereas our calculations have been for gas-phase species. A simple approach to taking into account the effects of the surroundings of a molecule is to employ the reaction-field model [34]. In this model, the solute is placed in a cavity in the solvent treated as a continuum of uniform dielectric constant. If the solute molecule has a dipole moment, a dipole will be induced in the surrounding solvent, which then interacts with the solute (through the reaction field) and stabilizes it. Approaches of this type differ in how the cavity and reaction field are defined. The isodensity polarized continuum model (IPCM) of Foresman and coworkers [35,36] places the cavity surface at a particular electron-density values of the solute molecule, and an enhanced version of this approach, the self-consistent isodensity polarized continuum model (SCIPCM), specifically takes into account the effects of solvation in the solution of the self-consistent field problem.

Table 8 shows data for these two types of reaction fields at several theoretical levels. The SCIPCM results are to be preferred and are more consistent. The indication is that phosphine oxide (OPH_3) is stabilized by 3–4 kcal/mol more than *anti*-phosphinous acid (PH_2OH). This is more than enough to swing the equilibrium of these two species toward the oxide by a factor of several hundred and clearly is the reason the hydroxide is not seen in aqueous solution.

TABLE 8 IPCM and SCIPCM Energy Lowerings for PH_2OH and OPH_3 in a polarized continuum of dielectric constant 78.39[a]

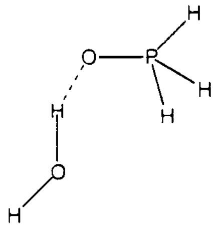
	$\Delta E = E_{gp} - E_{pcm}$		
	anti-PH_2OH	*OPH_3*	*$\Delta\Delta E$*
ICPM Model			
MP2/6-31+G(d,p)	−5.00	−9.94	−4.94
B3LYP/6-31+G(d,p)	−4.83	−10.56	−5.74
B3LYP/6-311++G(2d,p)	−4.12	−9.43	−5.31
SCICPM Model			
MP2/6-31+G(d,p)	−3.85	−7.35	−3.50
B3LYP/6-31+G(d,p)	−3.69	−7.26	−3.58
B3LYP/6-311++G(2d,p)	−3.24	−6.53	−3.29

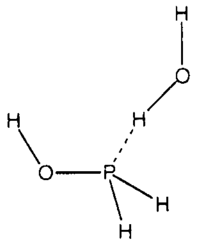
[a] $\Delta E = E_{gp} - E_{pcm}$. The optimized structures (in the gas phase) and the polarized continuum calculations were both carried out at the indicated levels. The energy data are in kcal/mol and represent the difference between the gas phase (gp) and the polarized continuum (pcm) energies, and the difference in these energy changes ($\Delta\Delta E$).

Now reaction field models are not thought to be appropriate for species where specific interactions such as hydrogen bonding can occur, an interaction clearly present for both OPH_3 and PH_2OH in water. In the oxide, one can expect three hydrogen bonds involving oxygen, and in phosphinous acid there will be two bonds involving oxygen and one involving phosphorus. The difference between the two, then, is basically the difference between a water-oxygen hydrogen bond and a water-phosphorus hydrogen bond. To estimate this difference, we performed B3LYP/6-311++G(3df,2p)//B3LYP/6-31+G(d,p) calculations on the dimers (the *anti* isomer of phosphinous acid) with one hydrogen bond each; the dimer dispositions employed are shown in Table 9. The monomer geometries were frozen at the B3LYP/6-31+G(d,p) optimized level with the H · · · O/H · · · P lengths and the H · · · OP/H · · · PO and OH · · · O/OH · · · P angles allowed to vary. Standard counterpoise corrections [37] were applied to the optimized structures.

Table 9 shows that the hydrogen bond in the ox-

TABLE 9 Geometrical Parameters and Electronic Energies for the Phosphine Oxide and Phosphinous Acid Molecules Hydrogen-Bonded to a Single Water Molecule[a]





	(H_2O)OPH_3	*anti-PH_2OH(H_2O)*
H···O/H···P	1.9045 Å	2.6359 Å
H···OP/H···PO	115.77°	132.25°
OH···O/OH···P	199.37°	195.00°
E (dimer)	−494.92254 au	−494.91671 au
E (monomer, cp)	−418.44802 au	−418.44863 au
E (H_2O, cp)	−76.46492 au	−76.46485 au
ΔE (cp corrected)	−0.00960 au	−0.00322 au
	(−6.03 kcal/mol)	(−2.02 kcal/mol)
$\Delta\Delta E = -4.00$ kcal/mol		

[a] The final energy differences have been counterpoise (cp) corrected.

ide is much shorter than that to phosphorus in phosphinous acid, and the water hydrogen bond to OPH_3 is stronger than that of water to PH_2OH by 4.00 kcal/mol. The water-oxide bond is expected to be stronger because of the dominant electrostatic nature of hydrogen bonds and the more electronegative nature of oxygen compared with phosphorus. This is only a representative estimate of the difference in overall hydrogen bond energies of the two species in aqueous solution, but the result is quite reasonable and in good agreement with the reaction field polarized continuum models. In both cases, the relative lowering of OPH_3 compared with PH_2OH is quite enough to move the equilibrium mainly to that favoring the oxide.

SUMMARY

High level ab initio quantum mechanical model chemistries have been used to study the relative stabilities of the simple phosphine oxides tautomers OPH_3/PH_2OH and $OPH(OH)_2/P(OH)_3$ and related molecules. It is found that the two PH_2OH isomers are virtually equi-energetic and only slightly more stable than OPH_3 itself, and the oxides with one or more hydroxyl groups are significantly more stable than their hydroxide tautomers. The difference in stability arises mainly from the variation of the $P=O$ bond energy among the various species; the $P=O$ bond energy increases with the number of hydroxyl groups present. The effects of solvation in aqueous solution are estimated by reaction field polarized continuum models and by explicit calculations of OPH_3 and PH_2OH hydrogen bound to a single water molecule. Both approaches indicate that the oxide form is significantly stabilized by its aqueous environment.

ACKNOWLEDGMENTS

I am indebted to the North Carolina Supercomputing Center for providing CPU time on the Cray T-916 and SGI Origin 2000 platforms that allowed these calculations to be performed and to Professor L. D. Quin for many helpful discussions.

REFERENCES

[1] Stawinski, J. In Handbook of Organophosphorus Chemistry; Engel, R., Ed.; Marcel-Dekker: New York, 1992, Chapter 8.
[2] Guthrie, J. P. Can J Chem 1979, 57, 236.
[3] Schmidt, M. W.; Yabushita, S.; Gordon, M. S. J Phys Chem 1984, 88, 382.
[4] Nguyen, M. T.; Hegarty, A. F. J Chem Soc Perkin Trans II 1987, 47.
[5] Schmidt, M. W.; Gordon, M. S. J Am Chem Soc 1985, 107, 1922.
[6] Schmidt, M. W.; Gordon, M. S. Can J Chem 1985, 63, 1909.
[7] MacDougall, P. J.; Hall, M. B. Trans Amer Cryst Assoc 1990, 26, 105.
[8] Reed, A. E.; Schleyer, P. v. R. J Am Chem Soc 1990, 112, 1434.
[9] Messmer, R. P. J Am Chem Soc 1991, 113, 433.
[10] Gilheany, D. G. In The Chemistry of Organophosphorus Compounds; Hartley, F. R., Ed.; Wiley and Sons: New York, 1992; Vol. 2, Chapter 1.
[11] Gilheany, D. G. Chem Rev 1994, 94, 1339.
[12] Chesnut, D. B. J Am Chem Soc 1998, 120, 10504.
[13] Dobado, H.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. J Am Chem Soc 1998, 120, 8461.
[14] Chesnut, D. B.; Savin, A. J Am Chem Soc 1999, 121, 2335.
[15] Withnall, R.; Andrews, L. J Phys Chem 1987, 91, 784.
[16] Curtiss, L. A.; Raghavachari, K.; Refern, P. C.; Rassolov, V.; Pople, J. A. J Chem Phys 1998, 109, 7764.
[17] Curtiss, L. A.; Refern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. J Chem Phys 1999, 110, 4703.
[18] Ochterski, J. W.; Petersson, G. A. J Chem Phys 1996, 104, 2598.
[19] Becke, A. D. J Chem Phys 1993, 98, 5648.
[20] Lee, C.; Yang, W.; Parr, R. G. Phys Rev 1988, B37, 785.
[21] Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Chem Phys Lett 1989, 157, 200.
[22] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.5; Gaussian, Inc., Pittsburgh, PA, 1998.
[23] Curtiss, L. A.; Raghavachari, K.; Pople, J. A. J Chem Phys 1993, 98, 1293.
[24] Bader, R. F. W. Acc Chem Res 1985, 18, 9.
[25] Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Clarendon Press: Oxford, 1990.
[26] Cioslowski, J.; Mixon, S. T. J Am Chem Soc 1991, 113, 4142.
[27] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.1 Gaussian, Inc., Pittsburgh, PA, 1995.
[28] (a) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J.

J Comput Chem 1996, 17, 49; (b) Peng, C.; Schlegel, H. B. Israel J Chem 1994, 33, 449.
[29] See, for example, Corbridge, D. E. C. Phosphorus: An Outline of its Chemistry, Biochemistry and Technology, 5th Ed.; Elsevier Scientific Publishing Co: New York, 1995; p 51–52.
[30] Keck, H.; Kuchen, W.; Schweighofer, A. Phosphorus Sulfur Silicon 1995, 104, 189.
[31] Cisolowski, J. Int J Quant Chem Quant Chem Symp 1990, 24, 15.
[32] Cisolowski, J. J Math Chem 1991, 8, 169.
[33] Bader, R. F. W.; Tang, T-H.; Tal, Y.; Biegler-Konig, F. W. J Am Chem Soc 1982, 104, 946.
[34] Onsager, L. J Am Chem Soc 1936, 58, 1486.
[35] Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. J Phys Chem 1996, 100, 16098.
[36] Foresman, J. B.; Frisch, A. Exploring Chemistry with Electronic Structure Methods, 2nd Ed.; Gaussian, Inc.: Pittsburgh, PA, 1996; Chapter 10.
[37] Boys, S. F.; Bernardi, F. Mol Phys 1970, 19, 553.