J. Phys. Chem. A **2006,** *110,* 8925−8932

Computational Study of the Thermochemistry of Organophosphorus(III) Compounds

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Received: February 15, 2006; In Final Form: May 12, 2006

The enthalpies of formation of organophosphorus(III) compounds have been calculated at the G3X, G3X(MP2), and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) levels of theory using the atomization energy procedure and the method of isodesmic reactions. The $\Delta_f H^\circ_{298}$ values for 50 relatively large molecules with up to 10 non-hydrogen atoms, such as $P(CH_3)_3$, $P(C_2H_5)_3$, $P(OCH_3)_3$, n-$C_4H_9OPCl_2$, $[(CH_3)_2N]_2PCl$, $(C_2H_5)_2NPCl_2$, and $[(CH_3)_2N]_2PCN$, have been calculated directly from the G3X atomization energies. A good agreement between the known experimental values and G3X results for 14 compounds provides support to our predictions for remaining species whose experimental enthalpies of formation are unknown or known with relatively large uncertainties. On the basis of our calculations and sometimes conflicting experimental data a set of internally consistent enthalpies of formation has been recommended for organophosphorus(III) compounds. Our computational results call into question the experimental enthalpies of formation of $P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$. From comparison with most reliable experimental data, the accuracy of the theoretical enthalpies of formation is estimated as ranging from 5 to 10 kJ/mol. The recommended $\Delta_f H^\circ_{298}$ values were used to derive the group additivity values (GAVs) for 45 groups involving the phosphorus(III) atom. These GAVs significantly extend the applicability of Benson's group additivity method and may be used to estimate the enthalpies of formation of larger organophosphorus(III) compounds, where high level quantum chemical calculations are impracticable.

Introduction

An important role of organophosphorus compounds in a variety of chemical processes, such as in biological systems, the synthesis of industrial chemicals, decomposition of pesticides and insecticides, destruction of chemical weapons, and catalytic applications leads to interest in their thermochemistry. Reliable thermochemical data are needed in thermodynamic modeling optimum conditions for chemical processes involving phosphorus compounds. The availability of accurate thermochemical data is of primary importance to solve the kinetic equations and the energy balances. Unfortunately, the experimental enthalpies of formation ($\Delta_f H^\circ_{298}$) for many important organophosphorus compounds are often unknown or only known with relatively large uncertainties. The problems in determining the enthalpy of formation of organophosphorus compounds arise from incomplete combustion and formation of a mixture of the various phosphorus oxy acids which make difficult the precise definition of the final system.[1] Besides, many of these compounds are hazardous and they can be difficult to handle in air. Because of the lack of accurate thermochemical data, alternative approaches, such as quantum chemical calculations or empirical group additivity method, should be used to predict the $\Delta_f H^\circ_{298}$ values for organophosphorus compounds. The empirical group additivity method of Benson[2−4] can predict the thermochemical properties of organic compounds with chemical accuracy, i.e., within 4 kJ/mol, if the experimental measurements on some key compounds were made with high accuracy. On the basis of reliable experimental data, the group additivity values (GAVs) were obtained for a large number of classes of organic compounds. However, only a few GAVs were determined for organophosphorus compounds,[3,5−8] and the group additivity scheme for these compounds was not developed until now because of the lack of precise experimental data. It therefore seems likely that predictions for the missing experimental thermochemical data of organophosphorus compounds can be derived from quantum chemical methods.

The enthalpies of formation of a series of phosphorus containing compounds with the number of non-hydrogen atoms up to five were calculated by Leroy et al.[9] using various ab initio methods adapted to the size of the species. The $\Delta_f H^\circ_{298}$ values for the small molecules were obtained from MP4/6-311++G(3df,2p)//MP2/6-31G(d,p) energies using hydrogenation reaction, whereas the $\Delta_f H^\circ_{298}$ values of large molecules were calculated at MP2/6-31G(d,p) level using isodesmic reactions. The calculated enthalpies of formation for two organic molecules, CH_3PH_2 and $P(CH_3)_3$, agree with experimental values within 5 kJ/mol. For other compounds considered by Leroy et al.,[9] the experimental data are not available.

The enthalpies of formation of small inorganic phosphorus molecules were recently calculated by Haworth and Bacskay[10] using the current methods of computational chemistry [CCSD(T), G3, G3X, and G3X2]. The authors have found that the G3X results reproduce the benchmark enthalpies of formation, on the average, to within ±8 kJ/mol. Lau and Li[11] have applied the G3 and G3X methods to study the thermochemistry of phosphorus fluorides PF_n ($n = 1−6$). On the basis of excellent agreement between the G3X and experimental results, a set of self-consistent thermochemical data was recommended for phosphorus fluorides and their ions.

As to organophosphorus molecules with six and more non-hydrogen atoms, the enthalpy of formation of $P(CN)_3$ was estimated by Gardner[12] from isogyric reactions using the MP2/6-311G(d,p) energies. The calculated value of $\Delta_f H^\circ_{298}[P(CN)_3,g] = 493$ kJ/mol was 76 kJ/mol lower than the

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10.1021/jp060982f CCC: $33.50

experimental value of 569 kJ/mol.[13] However, an even lower value (448 kJ/mol) was determined from new calorimetric sudy.[14] $P(CN)_3$ demonstrates how large errors in the experimental data for phosphorus containing compounds could be expected.

The most accurate quantum chemical methods, such as CCSD(T), are still only applicable to small molecules. To predict accurately thermochemical properties for larger molecules, the composite Gaussian-*n* [G2, G3, G3(MP2), G3X, G3X(MP2), etc.] methods were developed.[15−19] These methods use a series of high level correlation calculations [QCISD(T), MP4, CCSD(T)] with moderate sized basis sets to approximate the result of a more expensive calculations. The modification of the G3 theory, called Gaussian-3X (G3X), was designed to improve the agreement between theoretical and experimental enthalpies of formation for molecules, which contain second row atoms (Na−Ar). As mentioned above, this method gives a good agreement with experiment for inorganic phosphorus compounds.[10,11] In this work the G3X method was applied to calculate the enthalpies of formation of organic compounds containing tricoordinate phosphorus.

The aim of this study is (i) to assess generally accepted experimental data on organophosphorus(III) compounds using the G3X method, (ii) to recommend a set of consistent enthalpies of formation based on best quality experimental values and G3X results, (iii) to calculate accurate $\Delta_f H^\circ_{298}$ values for organophosphorus(III) compounds with the missing experimental thermochemical data, and (iv) to derive a consistent and accurate set of GAVs needed to estimate the enthalpies of formation of larger organophosphorus(III) molecules.

Computational Methods

All of the ab initio and density functional calculations were performed using the Gaussian 03 package of programs.[20] The composite G3X method is not implemented in the Gaussian 03 software and the G3X energies were calculated by combining the results of several different calculations as described by Curtiss et al.[19]

For many of organophosphorus compounds, the existence of rotational isomerism has been detected. To study the conformational behavior of such molecules, the initial calculations were made at the B3LYP/6-31G(d,p) level of density functional theory. The local minima and global minimum were located by inspection of the calculated torsional profile, and unconstrained optimizations were carried out to obtain the fully minimized structures. The B3LYP/6-31G(d,p) electronic energies, symmetry, and rotational constants for the most stable conformers of 55 target molecules are given in Table 1S of the Supporting Information.

The G3X energies were calculated for 50 compounds with the number of non-hydrogen atoms from 2 to 10. These energies were used to calculate the standard enthalpies of formation by the atomization energy approach.[21] This method involves the use of experimental enthalpies of formation of the gaseous atoms at 0 K and thermal corrections for elements in their standard states, whose values were taken from reference book by Gurvich et al.[22] (see also the Supporting Information, Table 2S). The $\Delta_f H^\circ_{298}$ values were calculated for the most stable conformer only. This assumption was used because the contribution of different conformers to the enthalpy is much smaller as compared to the difference between calculated and experimental $\Delta_f H^\circ_{298}$ values.

It is known that direct calculation of enthalpies of formation from quantum chemical atomization energies is often the subject of systematic errors arising from insufficient treatment of electron correlation and incompleteness of the basis sets. It has been suggested that the accumulation of these errors could be observed as the size of molecule increases. The systematic errors can be significantly reduced by using the isodesmic reactions,[23] in which the number of bonds of each type is conserved on the both sides of the reaction. An isodesmic reaction leads to more accurate results if the enthalpies of formation of reference compounds are determined with high accuracy, and if it is possible to chose the reaction with good group balance, where the next nearest neighbor interactions are also conserved. The performance of isodesmic reactions at several levels of theory, including ab initio, density functional theory, and composite methods (G2, G3, CBS-Q), has been systematically investigated in the publications of Bozzelli et al.[24−27] and Sumathi and Green.[28−30] The accuracy of enthalpies of formation predicted in these works ranges from 4 to 6 kJ/mol. In this work, the method of isodesmic reactions was used not only to check the reliability of G3X atomization energies but also to provide a double-check on the reasonableness of recommended enthalpies of formation of organophosphorus(III) compounds.

TABLE 1: Enthalpy of Formation of PH_3 Calculated from Atomization Energies and Isogyric Reactions (in kJ/mol)

reaction	G3X	G3X(MP2)	B3LYP/ 6-311+G(3df,2p)
atomization	10.3 (−4.9)[a]	7.1 (−1.7)	−9.2 (+14.6)
$PH_3 + 3HCl = PCl_3 + H_2$	8.8 (−3.4)	18.3 (−12.9)	−13.8 (+19.2)
$PH_3 + 3HF = PF_3 + H_2$	11.2 (−5.8)	16.7 (−11.3)	−6.1 (+11.5)

[a] Number in parentheses is the difference between the experimental (5.4 ± 1.7 kJ/mol, ref 1) and calculated values.

For five large molecules, $P[N(CH_3)_2]_3$, $P(OC_2H_5)_3$, $[(C_2H_5)_2N]_2PCl$, $P[OCH(CH_3)_2]_3$, and $P(C_6H_5)_3$, the computational resources requirement for G3X calculations is prohibitively high. For this reason, the G3X(MP2) method was used for $P[N(CH_3)_2]_3$, $[(C_2H_5)_2N]_2PCl$, and $P(OC_2H_5)_3$. The G3X(MP2) theory[19] is the modification of G3X theory. This method requires far less computational resources and has a reasonable accuracy. To evaluate the accuracy of G3X(MP2) method in predicting the enthalpies of formation, the calculations at this level of theory were also carried out for all compounds with known experimental data. For the two largest molecules, $P[OCH(CH_3)_2]_3$ and $P(C_6H_5)_3$, the electronic energies were calculated only at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level. These energies corrected by the B3LYP/6-31G(d,p) zero-point energies and the changes in enthalpy from 0 to 298 K were used to calculate the enthalpies of formation from isodesmic reactions. To estimate the reliability of this method, the calculations at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level were also performed for all 55 compounds considered in this work. The G3X, G3X(MP2), and B3LYP electronic energies, zero-point energies, and thermal corrections for 55 organophosphorus(III) compounds and 23 non-phosphorus species used in the isodesmic reactions are listed in Table 3S of the Supporting Information along with the enthalpies of formation for reference compounds. On the basis of the results of theoretical calculations and available experimental data, the $\Delta_f H^\circ_{298}$ values were recommended for all target compounds.

The results expected from the use of different approaches in estimating $\Delta_f H^\circ_{298}$ values are demonstrated in Table 1 with PH_3. As is seen, the values calculated from the G3X and G3X(MP2) atomization energies are in good agreement with experiment. Taking into account the rather large uncertainty of the experimental value, it is difficult to decide between two theories. As expected, the B3LYP method is unacceptable for

TABLE 2: Comparison of Experimental Enthalpies of Formation of Organophosphorus(III) Compounds with Values Calculated Using the Atomization Energy Method (in kJ/mol)

	calculation				
molecule	G3X	G3X(MP2)	experiment	recommended	Δ[a]
(**1**) $P(CH_3)_3$	−99.9	−102.5	−101.1 ± 5.2[b] −96.0 ± 4.0[c]	−101.1 ± 5.2	(+0.0)
(**2**) CH_3PH_2	−15.8	−18.7	−19.2 ± 6.3[d]	−19.5 ± 5.0	(+0.3)
(**3**) $(CH_3)_2PH$	−52.9	−55.2	−62.8[e]	−55.0 ± 5.0	(−7.8)
(**4**) $P(C_2H_5)_3$	−149.5	−151.5	−49.9 ± 12.8[b]	−150.0 ± 7.0	(+100.1)
(**5**) $P(C_6H_5)_3$	*f*	*f*	326.0 ± 12.0[c] 320.2 ± 4.7[b,g]	336.0 ± 10.0	(−10.0)
(**6**) *n*-$C_3H_7OPCl_2$	−491.8	−494.8	−487.5 ± 7.0[h]	−487.5 ± 7.0	(+0.0)
(**7**) *n*-$C_4H_9OPCl_2$	−513.0	−516.5	−507.7 ± 10.6[h]	−507.7 ± 5.0	(+0.0)
(**8**) $C_2H_5OPCl_2$	−469.6	−473.3	−461.1 ± 2.1[h]	−464.0 ± 5.0	(+2.9)
(**9**) CH_3OPCl_2	−433.1	−437.3	−418.2 ± 7.1[h]	−430.0 ± 5.0	(+11.8)
(**10**) $C_6H_5OPCl_2$	−307.0	−317.7	−309.8 ± 8.3[h]	−303.0 ± 7.0	(−6.8)
(**11**) $C_2H_5PCl_2$	−247.7	−254.9	−276.0 ± 16.0[b]	−248.0 ± 10.0	(−28.0)
(**12**) $P(OCH_3)_3$	−702.6	−694.5	−699.0 ± 8.0[c] −705.6 ± 6.2[b]	−699.0 ± 8.0	(+0.0)
(**13**) $P(OC_2H_5)_3$	*f*	−799.5	−808.0± 4.0[c] −813.4 ± 5.3[b]	−808.0 ± 4.0	(+0.0)
(**14**) $P[OCH(CH_3)_2]_3$	*f*	*f*	−925.0 ± 8.0 −933.7 ± 9.4[b]	−925.0 ± 8.0	(+0.0)
(**15**) $(CH_3)_2NPCl_2$	−232.8	−236.4	−245.5 ± 2.5[i] −246.0 ± 2.0[c]	−235.0 ± 7.0	(−10.5)
(**16**) $[(CH_3)_2N]_2PCl$	−159.7	−157.1	−174.2 ± 2.6[i] −174.0 ± 2.0[c]	−162.0 ± 10.0	(−12.2)
(**17**) $(C_2H_5)_2NPCl_2$	−291.4	−294.4	−304.0 ± 7.0[j] −388.0 ± 7.0[b]	−294.0 ± 10.0	(−10.0)
(**18**) $[(C_2H_5)_2N]_2PCl$	*f*	−266.3	−282.0 ± 10.0[b]	−263.0 ± 10.0	(−19.0)
(**19**) $P(CN)_3$	470.0	468.3	452.0 ± 25.0[c] 448.4 ± 7.4[l] 568.6 ± 25.1[k]	470.0 ± 10.0	(−18.0)
(**20**) $(CH_3)_2NP(CN)_2$	259.6	262.2	249.0 ± 16.0[c] 228.7 ± 5.5[l]	260.0 ± 10.0	(−11.0)
(**21**) $[(CH_3)_2N]_2PCN$	82.6	88.1	65.0 ± 8.0[c] 54.2 ± 3.5[l]	83.0 ± 7.0	(−18.0)
(**22**) $P[N(CH_3)_2]_3$	*f*	−57.9	−71.3 ± 2.4[i] −71.0 ± 2.0[c]	−62.0 ± 10.0	(−9.3)
(**23**) $P(n\text{-}C_4H_9)_3$			−54.0 ± 35.0[b]	−276.0 ± 10.0[m]	(+222.0)
(**24**) $P[N(C_2H_5)_2]_3$			−222.0 ± 13.0[c] −225.6 ± 10.5[b]	−222.0 ± 10.0	(+0.0)

[a] Deviation of recommended value from experiment. [b] Reference 1. [c] Reference 31. [d] Reference 34. [e] Wada Y. Ph.D. thesis; cited from ref 35. [f] The G3X calculation for this molecule is beyond our computational possibilities. [g] Reference 36. [h] Reference 32. [i] Reference 33. [j] This value was calculated from $\Delta_f H°$(liq) and $\Delta_{vap}H°$ given in ref 1 (see text). [k] Reference 13. [l] Reference 14. [m] Calculated from group additivity values; see Table 4 and text.

the estimation by atomization energy procedure. The key to success in use of isodesmic reactions is to find processes in which the initial reactants and final products are as similar as possible.[23] In this case the energies of isodesmic reactions are generally well described using even the simple computational method. Although the total number of electron pairs is conserved in the isogyric reactions in Table 1, significant differences in bonding exist between reactant and product molecules. Because of this, only at the G3X level of theory do these reactions lead to reasonable estimation of the enthalpy of formation of PH_3. Further, it will shown that reliable results could also be obtained at the G3X(MP2) and B3LYP level if the more appropriate reactions are used. In such isodesmic reactions, not only the number of bonds of each type is conserved but also their nearest environment.

The recommended $\Delta_f H^\circ_{298}$ values were used to derive a set of consistent GAVs that could be applied in the prediction of unknown enthalpies of formation of organophosphorus(III) compounds. The terms involving the phosphorus atom were obtained by means of the least-squares method. These GAVs have been applied to check the reliability of published experimental data for two large molecules, whose theoretical calculations were not performed in this work.

Results and Discussion

Assessment of the Experimental Results. The experimental enthalpies of formation of 22 compounds were obtained from several sources, including the review of thermochemical properties by Pilcher[1] and Rabinovich et al.,[31] and more recent experimental measurements.[14,32,33] These experimental data together with the results of G3X and G3X(MP2) calculations by the atomization energy approach are given in Table 2. The list of isodesmic reactions used for each molecule is compiled in Table 3 with the corresponding enthalpies of formation and enthalpies of reactions ($\Delta_f H^\circ_{298}$) calculated at the G3X and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) levels. In this part, by comparing the G3X, G3X(MP2), and B3LYP results with sometimes conflicting experimental data, a set of internally consistent $\Delta_f H^\circ_{298}$ values is recommended for organophosphorus(III) compounds.

The first molecule to be tested was the $P(CH_3)_3$ (**1**). As is seen from Table 2, the experimental enthalpies of formation of this molecule are in excellent agreement with the values calculated from G3X and G3X(MP2) atomization energies. The experimental value of −101.1 kJ/mol was adopted in this work and it was thereafter used in the isodesmic reaction calculations. The isodesmic reactions may also be designed for $P(CH_3)_3$ itself

TABLE 3: Enthalpies of Formation of Organophosphorus(III) Compounds Calculated from Isodesmic Reactions (in kJ/mol)

	B3LYP		G3X	
isodesmic reaction[a]	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$
(**1**) $P(CH_3)_3 + PH_3 = CH_3PH_2 + (CH_3)_2PH$	13.4	−87.5	20.9	−95.0
$P(CH_3)_3 + 3C_3H_8 = P(C_2H_5)_3 + 3\ C_2H_6$	22.9	−109.7	11.7	−98.5
(**2**) $3CH_3PH_2 = P(CH_3)_3 + 2PH_3$	−6.9	−23.2	−10.6	−19.5
(**3**) $3(CH_3)_2PH = 2P(CH_3)_3 + PH_3$	−6.5	−59.1	−10.3	−55.3
(**4**) $P(C_2H_5)_3 + 3C_3H_8 = P(CH_3)_3 + 3C_4H_{10}$	−21.8	−142.3	−13.1	−151.0
(**5**) $P(C_6H_5)_3 + 2PH_3 = 3C_6H_5PH_2$	11.5	354.8		
$P(C_6H_5)_3 + C_6H_5C_2H_5 + C_4H_{10} = P(C_2H_5)_3 + 2C_6H_5C_6H_5$	−26.7	336.4		
$P(C_6H_5)_3 + 3C_2H_6 = P(CH_3)_3 + 3C_6H_5CH_3$	−41.4	343.2		
(**6**) $n\text{-}C_3H_7OPCl_2 + CH_3Cl = n\text{-}C_3H_7OCH_3 + PCl_3$	48.6	−491.0	56.0	−498.4
(**7**) $n\text{-}C_4H_9OPCl_2 + C_3H_8 = n\text{-}C_3H_7OPCl_2 + C_4H_{10}$	−0.1	−508.4	0.3	−508.8
$n\text{-}C_4H_9OPCl_2 + CH_3Cl = n\text{-}C_4H_9OCH_3 + PCl_3$	48.7	−511.1	56.2	−518.6
(**8**) $C_2H_5OPCl_2 + C_5H_{12} = n\text{-}C_4H_{10}OPCl_2 + C_3H_8$	−0.1	−465.4	−1.7	−463.8
$C_2H_5OPCl_2 + C_4H_{10} = n\text{-}C_3H_7OPCl_2 + C_3H_8$	0.2	−466.7	−1.3	−465.2
(**9**) $CH_3OPCl_2 + C_2H_5OCH_3 = C_2H_5OPCl_2 + CH_3OCH_3$	−1.7	−434.0	−2.0	−429.7
$CH_3OPCl_2 + n\text{-}C_3H_7OCH_3 = n\text{-}C_3H_7OPCl_2 + CH_3OCH_3$	−2.7	−430.8	−3.4	−430.1
$CH_3OPCl_2 + n\text{-}C_4H_9OCH_3 = n\text{-}C_4H_9OPCl_2 + CH_3OCH_3$	−2.8	−430.9	−3.7	−430.0
(**10**) $C_6H_5OPCl_2 + CH_3Cl = C_6H_5Cl + CH_3OPCl_2$	1.6	−297.7	5.9	−302.0
$C_6H_5OPCl_2 + C_3H_8 = C_6H_5C_2H_5 + CH_3OPCl_2$	6.2	−301.5	8.0	−303.3
$C_6H_5OPCl_2 + n\text{-}C_5H_{12} = n\text{-}C_3H_7OPCl_2 + C_6H_5C_2H_5$	−9.7	−300.9	−9.0	−301.6
$C_6H_5OPCl_2 + C_3H_8 = C_6H_5CH_3 + C_2H_5OPCl_2$	−11.3	−297.5	−6.8	−302.3
$C_6H_5OPCl_2 + n\text{-}C_5H_{12} = n\text{-}C_4H_9OPCl_2 + C_6H_5CH_3$	−11.4	−298.9	−8.4	−305.2
(**11**) $C_2H_5PCl_2 + CH_3PH_2 = CH_3PCl_2 + C_2H_5PH_2$	−2.2	−240.8	−1.0	−244.0
$C_2H_5PCl_2 + C_2H_6 = CH_3PCl_2 + C_3H_8$	−4.8	−243.6	−0.3	−248.1
$C_2H_5PCl_2 + CH_3Cl = PCl_3 + C_3H_8$	−56.9	−252.1	−51.0	−258.0
(**12**) $P(OCH_3)_3 + 2CH_3Cl = CH_3OPCl_2 + 2CH_3OCH_3$	36.8	−671.2	57.8	−692.2
(**13**) $P(OC_2H_5)_3 + 3C_2H_6 = P(OCH_3)_3 + 3C_3H_8$	40.4	−802.1	43.3[b]	−805.0[b]
(**14**) $P[OCH(CH_3)_2]_3 + 3C_2H_6 = P(OC_2H_5)_3 + 3C_3H_8$	33.5	−904.2		
$P[OCH(CH_3)_2]_3 + 3C_2H_6 = P(OCH_3)_3 + 3(CH_3)_3CH$	62.8	−913.0		
(**15**) $(CH_3)_2NPCl_2 + CH_3Cl = (CH_3)_3N + PCl_3$	7.0	−234.9	13.4	−241.3
$(CH_3)_2NPCl_2 + C_2H_5OH = (CH_3)_2NH + C_2H_5OPCl_2$ (16)	−25.1	−222.5	−16.9	−230.7
(**16**) $[(CH_3)_2N]_2PCl + 2CH_3Cl = 2(CH_3)_3N + PCl_3$	−22.9	−146.7	−4.5	−165.1
$[(CH3)_2N]_2PCl + CH_3Cl = (CH_3)_2NPCl_2 + (CH_3)_3N$	−30.0	−146.7	−17.9	−158.8
(**17**) $(C_2H_5)_2NPCl_2 + 2C_2H_6 = (CH_3)_2NPCl_2 + 2C_3H_8$	6.7	−283.5	17.8	−294.6
$(C_2H_5)_2NPCl_2 + C_2H_5Cl = (C_2H_5)_3N + PCl_3$	24.2	−291.0	29.7	−296.5
(**18**) $[(C_2H_5)_2N]_2PCl + 2C_2H_5Cl = 2(C_2H_5)_3N + PCl_3$	0.5	−247.9	15.0[b]	−262.4[b]
$[(C_2H_5)_2N]_2PCl + 4C_2H_6 = [(CH_3)_2N]_2PCl + 4C_3H_8$	2.5	−248.1	26.8[b]	−272.4[b]
$[(C_2H_5)_2N]_2PCl + C_2H_6 + CH_3Cl = (CH_3)_2NPCl_2 + C_3H_8 + (C_2H_5)_3N$	−27.0	−239.7	−3.3[b]	−263.4[b]
(**19**) $P(CN)_3 + P(CH_3)_3 = (CH_3)_2PCN + CH_3P(CN)_2$	−66.9	477.6	−61.7	472.3
(**20**) $(CH_3)_2NP(CN)_2 + PCl_3 + HCN = P(CN)_3 + (CH_3)_2NPCl_2 + HCl$	34.7	262.2	3.2	265.3
(**21**) $[(CH_3)_2N]_2PCN + CH_3CN = (CH_3)_2NP(CN)_2 + (CH_3)_3N$	72.5	89.9	80.7	81.7
$[(CH_3)_2N]_2PCN + 2CH_3CN = 2(CH_3)_3N + P(CN)_3$	181.9	92.9	194.8	80.0
(**22**) $P[N(CH_3)_2]_3 + PH_3 = H_2PN(CH_3)_2 + HP[N(CH_3)_2]_2$	15.9	−33.6	42.9[b]	−60.5[b]
$P[N(CH_3)_2]_3 + PCl_3 = [(CH_3)_2N]_2PCl + (CH_3)_2NPCl_2$	−64.7	−43.1	−50.2[b]	−59.6[b]
$P[N(CH_3)_2]_3 + P(CN)_3 = [(CH_3)_2N]_2PCN + (CH_3)_2NP(CN)_2$	−73.4	−53.6	−60.1[b]	−66.9[b]

[a] Numbers in parentheses correspond to molecule's numbers in Table 2. The values of enthalpies of reactions, $\Delta_r H^\circ_{298}$, are given together with enthalpies of formation, $\Delta_f H^\circ_{298}$, for each reaction. The enthalpies of formation of all reference species are given in Table 3S of the Supporting Information. [b] Value is calculated using G3X(MP2) energies.

(Table 3). At this step, in these reactions the G3X values were accepted for the enthalpies of formation of $CH_3{-}PH_2$, $(CH_3)_2PH$, and $P(C_2H_5)_3$, because their experimental values are rather uncertain. As can be seen, the two isodesmic reactions with G3X energies give the close values, which are in good agreement with experiment, whereas the use of B3LYP energies leads to large difference in the results for the same reactions. For comparison, the value of −105.7 kJ/mol was estimated for $P(CH_3)_3$ by Leroy et al.[9] using isodesmic reactions at the MP2/6-31G(d,p) level of theory.

The experimental data for molecules **2** and **3** may be not reliable enough: the first value was estimated from data on electronegativity[34] and the second one was not published in accessible source of information. For these molecules, the values calculated from the G3X energies by isodesmic reactions method (Table 3) are recommended. We always preferred this method for well-balanced reactions with accurately measured enthalpies of formation of reference species, because, as noted above, this should result in a more effective cancellation of systematic errors. The value of $\Delta_f H^\circ_{298}(CH_3PH_2,g) = -23.6$ kJ/mol was calculated by Leroy et al.[9] from hydrogenation reaction at the MP4/6-311++G(3df,2p)//MP2/6-31G(d,p) level. As is seen, this value is very close to that obtained from isodesmic reaction at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level (Table 3), however, somewhat less than values estimated from G3X and G3X(MP2) calculations.

From calculations at the different levels of theory, it may be concluded that the experimental $\Delta_f H^\circ_{298}$ value for $P(C_2H_5)_3$ (**4**) is in error. Almost the same values were calculated using the atomization scheme and isodesmic reaction with G3X energies; their average value is recommended in Table 2. The recommended value is also supported by the group additivity method. The molecule $P(C_2H_5)_3$ differs from $P(CH_3)_3$ by adding three CH_2 groups. Using the value of −20.9 kJ/mol[37] for the [C−(C)2-(H)2] group, it can be approximately estimated that the enthalpy of formation of $P(C_2H_5)_3$ should be about 60 kJ/mol more negative than that of $P(CH_3)_3$, whereas the experimental $\Delta_f H^\circ_{298}$ value for **4** is 50 kJ/mol more positive than that for **1**.

The enthalpy of formation of molecule $P(C_6H_5)_3$ (**5**) with 19 non-hydrogen atoms could be calculated only at the B3LYP level of theory using isodesmic reactions. Three isodesmic reactions in Table 3 give the $\Delta_f H^\circ_{298}$ values which are from 10 to 35 kJ/mol larger than the experimental ones. Despite better group balance, the first isodesmic reaction may lead to overestimated value as it includes three $C_6H_5PH_2$ molecules for which the G3X enthalpy of formation was used instead of unknown experimental data. The value obtained from second isodesmic reaction is recommended in Table 2. As is seen, this value agrees with experimental value of 326 ± 12 kJ/mol[31] within its uncertainty.

For molecule **6**, the enthalpy of formation calculated from G3X atomization energy (Table 2) is in close agreement with experimental value, whereas the value calculated using isodesmic reaction at the G3X level (Table 3) is ~10 kJ/mol less. However, the isodesmic reaction for this molecule appears to be not enough well-balanced to motivate the revision of experimental value. The enthalpies of formation calculated for **7** from G3X and G3X(MP2) atomization energies are slightly more negative than experimental one (Table 2). However, the B3LYP and G3X values from first especially well-balanced isodesmic reaction with $\Delta_r H^\circ_{298} \approx 0$ are close to each other and to experimental value. The latter is recommended in this work.

In general, all calculated values for molecules **8** and **10** are in good agreement with experiment. Nevertheless, their values were somewhat improved (Table 2) taking into account consistent results for both types of well-balanced isodesmic reactions (Table 3). Different methods lead to more negative $\Delta_f H^\circ_{298}$ values for molecule **9** compared to experiment. The value recommended in this work is based on the results of isodesmic reaction method applied to both G3X and B3LYP energies. The $\Delta_f H^\circ_{298}$ value calculated from G3X atomization energy is adopted in this work for **11**. The values obtained using first two isodesmic reactions (Table 3) are in good agreement with recommended one, even though theoretical G3X enthalpies of formation are used for CH_3PCl_2 and $C_2H_5PH_2$.

The experimental $\Delta_f H^\circ_{298}$ values are not revised for molecules **12** and **13**. The overall good agreement between calculated and experimental values is observed for these molecules. For **14**, the theoretical estimates are obtained only at the B3LYP level using isodesmic reactions. As the uncertainties in the computed $\Delta_f H^\circ_{298}$ values are comparable to discrepancy between experiment and theory, the experimental value is recommended for this molecule. On the basis of the G3X values obtained by the atomization energy approach and isodesmic reaction method, the adopted enthalpies of formation of **15** and **16** are ~10 kJ/mol higher than the experimental values. The experimental value of $\Delta_f H^\circ_{298} = -388$ kJ/mol given for $(C_2H_5)_2NPCl_2$ (**17**) in the review by Pilcher[1] is likely to be a typographical error. The value of −304.4 kJ/mol may be calculated from values of $\Delta_f H^\circ(\text{liq}) = -345.7$ kJ/mol and $\Delta_{\text{vap}} H^\circ = 42$ kJ/mol given in Table 1 of the ref 1. However, even this value is about 10 kJ/mol lower than those calculated by different methods (Tables 2 and 3). The recommended value is based on the results of the G3X calculations using both the atomization energy and isodesmic reaction methods.

On the basis of the results from two most balanced isodesmic reactions with G3X(MP2) energies (first and third reactions in Table 3), the enthalpy of formation of molecule **18** is accepted to be ~20 kJ/mol larger than the available experimental value. This value is also close to the result from G3X(MP2) atomization energy. Examining the results of Table 2, it can be found that all of the calculated G3X(MP2) values are well within 10 kJ/mol of well-established experimental data. Hence, it may be believed that the G3X(MP2) result gives a more reliable value of enthalpy of formation of **18** compared to experiment. The large uncertainty in the experimental $\Delta_f H^\circ_{298}$ values of $P(CN)_3$ (**19**) was discussed in the Introduction. The enthalpies of formation calculated in Tables 2 and 3 are about 20 kJ/mol larger than the more recent experimental value. Because different methods for computing enthalpy of formation give very close results, the theoretical value is recommended in this work for $P(CN)_3$.

The two experimental enthalpies of formation for **20** are rather different. The $\Delta_f H^\circ_{298}$ value calculated from G3X atomization energy is recommended for this molecule. The accepted value is in good agreement with that calculated from isodesmic reaction. All theoretical methods predict the enthalpies of formation of molecule **21** to be larger than both experimental values. Our recommended value based on G3X atomization energy is in good agreement with those calculated from isodesmic reactions with G3X energies. The G3X(MP2) results obtained by both methods for **22** are about 10 kJ/mol larger than the experimental value. The discrepancies with values calculated from the B3LYP isodesmic reactions are still more. The value adopted in Table 2 is the average from the results of isodesmic reactions applied to G3X(MP2) energies.

The accuracy of G3X enthalpies of formation for small inorganic phosphorus compounds was estimated as ranging from 4 to 10 kJ/mol.[10] The available experimental values for organophosphorus(III) compounds cannot be properly assessed because their uncertainties are sometimes quite large. Nevertheless, examining the results given in Table 2, it can be seen that the recommended values agree with available experimental data within 10 kJ/mol for 14 from 22 compounds. Therefore, the supporting evidence for high accuracy of G3X theory for phosphorus compounds comes from our results. The experimental data for these compounds (**1**−**3**, **5**−**8**, **10**, **12**−**15**, **17**, **22**) appear to be the most reliable among those given in Table 2. The difference between experimental and recommended values for 7 compounds is in the range of 11−28 kJ/mol. Most likely the experimental data for these compounds are not enough reliable and theoretical results should be preferred. An exceedingly large difference between experimental and calculated values for **4** points to incorrect experimental measurements for this compound.

The information in Tables 2 and 3 allows one to evaluate the performance of the different methods in predicting the enthalpies of formation. Although the mean difference between the G3X and G3X(MP2) results is only 4.1 kJ/mol, the mean absolute deviation of G3X results from recommended values is 2.4 kJ/mol compared to 4.6 kJ/mol for G3X(MP2). As one would expect, the G3X method has the advantage compared to G3X(MP2) theory.

To check the accumulation of systematic errors in the atomization scheme for large molecules, the $\Delta_f H^\circ_{298}$ values calculated at the G3X level from well-balanced isodesmic reactions (molecules **4**, **7**−**10**, **16**, **17**, **20**) were compared with those obtained from G3X atomization energies. The discrepancies between these values are different in sign and do not exceed 6 kJ/mol. Because of possible uncertainties in the $\Delta_f H^\circ_{298}$ values of phosphorus containing species used in the isodesmic reactions as reference molecules, it is difficult to establish whether these discrepancies are due to accumulation of errors. In any event, the accumulated systematic errors are relatively small.

The importance of well-balanced isodesmic reactions for determining accurate enthalpies of formation is illustrated by reactions for molecules **7**−**11** in Table 3. As can be seen, these

TABLE 4: Enthalpies of Formation Organophosphorus(III) Compounds Calculated from G3X Atomization Energies Compared with Values Estimated by the Group Additivity Method (in kJ/mol)

molecule[a]	G3X[b]	GA	Δ[c]
(**1**) P(CH$_3$)$_3$	−101.1	−100.5	(−0.6)
(**2**) CH$_3$PH$_2$	−19.5	−19.3	(−0.2)
(**3**) (CH$_3$)$_2$PH	−55.0	−55.0	
(**4**) P(C$_2$H$_5$)$_3$	−150.0	−150.6	(+0.6)
(**5**) P(C$_6$H$_5$)$_3$	336.0	336.0	
(**6**) *n*-C$_3$H$_7$OPCl$_2$	−487.5	−486.0	(−1.5)
(7) *n*-C$_4$H$_9$OPCl$_2$	−507.7	−506.9	(−0.8)
(**8**) C$_2$H$_5$OPCl$_2$	−464.0	−465.1	(+1.1)
(**9**) CH$_3$OPCl$_2$	−430.0	−431.2	(+1.2)
(**10**) C$_6$H$_5$OPCl$_2$	−303.0	−303.0	
(**11**) C$_2$H$_5$PCl$_2$	−248.0	−246.1	(−1.9)
(**12**) P(OCH$_3$)$_3$	−699.0	−704.9	(+5.9)
(**13**) P(OC$_2$H$_5$)$_3$	−808.0	−806.6	(−1.4)
(**14**) P[OCH(CH$_3$)$_2$]$_3$	−925.0	−920.6	(−4.4)
(**15**) (CH$_3$)$_2$NPCl$_2$	−235.0	−236.2	(+1.2)
(**16**) [(CH$_3$)$_2$N]$_2$PCl	−162.0	−159.2	(−2.8)
(**17**) (C$_2$H$_5$)$_2$NPCl$_2$	−294.0	−292.8	(−1.2)
(**18**) [(C$_2$H$_5$)$_2$N]$_2$PCl	−263.0	−265.8	(+2.8)
(**19**) P(CN)$_3$	470.0	470.0	
(**20**) (CH$_3$)$_2$NP(CN)$_2$	260.0	260.0	
(**21**) [(CH$_3$)$_2$N]$_2$PCN	83.0	83.0	
(**22**) P[N(CH$_3$)$_2$]$_3$	−62.0	−62.0	
C$_2$H$_5$PH$_2$	−34.9	−36.0	(+1.1)
(CH$_3$)$_2$PPH$_2$	−40.2	−40.2	
n-C$_3$H$_7$PH$_2$	−57.4	−56.9	(−0.5)
i-C$_3$H$_7$PH$_2$	−59.9	−59.9	
n-C$_4$H$_9$PH$_2$	−78.2	−77.8	(−0.4)
(CH$_3$)$_3$CPH$_2$	−93.0	−93.0	
C$_6$H$_5$PH$_2$	125.7	125.7	
CH$_3$PCl$_2$	−227.5	−229.4	(+1.9)
CH$_3$PHCl	−113.2	−113.2	
(CH$_3$)$_2$PCl	−169.3	−169.3	
CH$_3$OPH$_2$	−183.0	−183.0	
(CH$_3$)$_2$POH	−308.4	−308.4	
(CH$_3$)$_2$POCH$_3$	−279.5	−279.5	
CH$_3$NHPH$_2$	10.9	10.9	
CH$_3$PHNH$_2$	−38.8	−38.8	
H$_2$PCH$_2$PH$_2$	31.1	31.1	
H$_2$C=PH	117.2	117.2	
(CH$_3$)$_2$NPH$_2$	13.1	13.1	(+0.0)
(CH$_3$)PNH$_2$	−91.7	−91.7	
CH$_3$P(CN)$_2$	247.9	247.9	
(CH$_3$)$_2$PCN	61.6	61.6	
[(CH$_3$)$_2$N]$_2$PH	−25.4	−25.4	
CH$_3$PF$_2$	−645.2	−645.2	
CH$_3$PHF	−302.5	−302.5	
(CH$_3$)$_2$PF	−361.9	−361.9	
(CH$_3$)$_2$NPF$_2$	−667.4	−667.4	
F$_2$PCN	439.5	439.5	
CH$_3$OPF$_2$	−878.7	−878.7	
CH$_3$SPCl$_2$	−219.9	−219.9	
CH$_3$SPF$_2$	−636.4	−636.4	
CH$_3$SPH$_2$	−8.8	−8.8	
(CH$_3$)$_2$PSH	−87.5	−87.5	
(CH$_3$)$_2$PSCH$_3$	−97.5	−97.5	
(NH$_2$)$_2$PCl	−178.8	−178.8	(+0.0)
(**23**) P(*n*-C$_4$H$_9$)$_3$		−276.0	
(**24**) P[N(C$_2$H$_5$)$_2$]$_3$		−221.9	

[a] Numbers in parentheses correspond to molecule's numbers in Table 2. [b] For 22 numbered molecules, the values recommended on the basis of G3X calculations are given (see Table 2). [c] Δ is the difference between G3X and GA enthalpies of formation; these differences are not given for molecules with one unique group, whose value is adjusted so as to reproduce the G3X value.

TABLE 5: GAVs for Phosphorus Containing Groups Derived from Experimental Data and G3X Calculations (in kJ/mol)

group	value
C−(X)(H)3[a]	−41.80[b]
C−(C)2(H)2	−20.90[b]
C−(C)(O)(H)2	−33.90[b]
C−(C)2(O)(H)	−30.10[b]
C−(C)(N)(H)2	−28.30[c]
Cb−(H)	13.80[b]
Cb−(O)	−3.80[b]
gauche correction[d]	3.30[b]
C−(P)(C)(H)2	−16.68
C−(P)(C)2(H)	1.21[e]
C−(P)(C)3	32.40[e]
C−(P)2(H)2	8.61[e]
Cb−(P)	3.30
P−(C)(H)2	22.49
P−(C)2(H)	28.60[e]
P−(C)3	24.87
P−(C)(H)(Cl)	−71.40[e]
P−(C)(Cl)2	−187.61
P−(C)2(Cl)	−85.70[e]
P−(C)(H)(F)	−260.70[e]
P−(C)(F)2	−603.40[e]
P−(C)2(F)	−278.30[e]
P−(O)(C)2	16.18
P−(O)(H)2	29.08[e]
P−(O)3	−68.64
P−(O)(Cl)2	−219.12
P−(O)(F)2	−666.62[e]
P−(N)(H)2	30.03
P−(N)2(H)	1.89[e]
P−(N)(C)(H)	26.42[e]
P−(N)(C)2	15.32[e]
P−(N)(Cl)2	−219.27
P−(N)(F)2	−650.47[e]
P−(N)2(Cl)	−131. 94
P−(N)3	−21.11[e]
P−(C)2(CN)	145.20[e]
P−(C)(CN)2	289.73[e]
P−(N)(CN)2	276.93[e]
P−(N)2(CN)	110.26[e]
P−(Cb)(H)2	53.40[e]
P−(Cb)3	119.09[e]
P−(S)(H)2	146.33[e]
P−(S)(C)2	141.23
P−(S)(Cl)2	−64.77[e]
P−(S)(F)2	−481.27[e]
O−(P)(H)	−240.98[e]
O−(P)(C)	−170.28
O−(P)(Cb)	−149.08[e]
S−(P)(H)	−145.13[e]
S−(P)(C)	−113.33
N−(P)(H)2	−23.42
N−(P)(C)(H)	22.67[e]
N−(P)(C)2	66.67

[a] X = C, O, N, S, P. [b] Reference 37. [c] Reference 38. [d] Nonnearest neighbor 1,4-interaction in amines. [e] The value calculated on single molecule containing this group.

especially well-balanced reactions lead to very close results regardless of the level of theory. As noted above, the needed $\Delta_f H^\circ_{298}$ values for organophosphorus(III) compounds are often known with large uncertainty or not available at all. Because of this, the G3X enthalpies of formation calculated from atomization energies were used sometimes for such molecules instead of experimental data. It is obvious that in this case the accuracy of prediction by isodesmic reaction method is reduced and then the estimation from atomization energy can lead to better result. Alternatively, the preference should be given to isodesmic reactions if they give consistent results with different reference molecules, as it was, for example, for C$_6$H$_5$OPCl$_2$ (**10**). Overall, the isodesmic reactions from Table 3 demonstrate the consistency of enthalpies of formation recommended in Table 2.

Group Additivity Values (GAVs). By comparison of the experimental data with the G3X results in our previous discussion, it was determined that the G3X method gives sufficiently accurate enthalpies of formation for organophosphorus(III) compounds. Therefore, the G3X enthalpies of formation calculated by atomization energy scheme can be used instead of experimental values to obtain the GAVs. Thus, in addition to molecules from Table 2, the $\Delta_f H^\circ_{298}$ values were also calculated for 33 organophosphorus(III) compounds, whose experimental data are not available. The calculated values for these molecules are given in Table 4, where the previously studied 22 molecules are also included. All these $\Delta_f H^\circ_{298}$ values were used to derive the GAVs. A total of 45 phosphorus containing groups are listed in Table 5 together with non-phosphorus groups taken from literature.[37,38] The most part of GAVs was obtained from a single compound. However, it is not to be supposed that these values can be subject to large uncertainties. As is seen from Table 2, the G3X enthalpies of formation are very close to values recommended from comparison of experimental data with theoretical results obtained by different methods. We believe that the uncertainties of the $\Delta_f H^\circ_{298}$ values calculated from GAVs may range from 5 to 15 kJ/mol. A good agreement between the enthalpies of formation recommended in this work and those calculated from GAVs is shown in Table 4.

The derived GAVs were used to calculate the enthalpies of formation of two large molecules **23** and **24**, whose experimental data are known from literature (Table 2), but their quantum chemical calculations were not performed in this work. The $\Delta_f H^\circ_{298}$ value calculated for **24** is in excellent agreement with experiment. However, the calculated enthalpy of formation for **23** is 222 kJ/mol more negative than experimental value. The value calculated from GAVs is recommended in Table 2 for molecule **23**. The large error in the experimental data for molecules **23** may be also demonstrated using the simple group additivity principles. The molecule $P(n\text{-}C_4H_9)_3$ (**23**) differs from $P(CH_3)_3$ (**1**) and $P(C_2H_5)_3$ (**4**) by adding nine and six CH_2 groups, respectively. Hence, using the value of −20.9 kJ/mol[37] for the [C−(C)2(H)2] group it can be obtained that the enthalpy of formation of $P(n\text{-}C_4H_9)_3$ should be about 188 and 125 kJ/mol more negative than those of $P(CH_3)_3$ and $P(C_2H_5)_3$, respectively This result is inconsistent with the experimental $\Delta_f H^\circ_{298}$ values of **4** and **23**, which are nearly equal and more positive than the $\Delta_f H^\circ_{298}$ value for $P(CH_3)_3$. Thus, both theoretical and empirical estimations indicate that experimental data for molecules $P(C_2H_5)_3$ (**4**) and $P(n\text{-}C_4H_9)_3$ (**23**) are incorrect and should be remeasured.

Conclusions

The enthalpies of formation of 55 organophosphorus(III) compounds have been calculated at the G3X, G3X(MP2), and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) levels of theory using the atomization energy procedure and the method of isodesmic reactions. The $\Delta_f H^\circ_{298}$ values for 50 moderate sized molecules with 2−10 non-hydrogen atoms have been calculated directly from the G3X atomization energies. By comparison of the available experimental data with the G3X results, it was found that the G3X method succeeded in reproducing well-established enthalpies of formation to an accuracy of ±10 kJ/mol. A good agreement between the known experimental values and G3X results for 14 compounds provides support to our predictions for remaining species whose experimental enthalpies of formation are unknown or known with large uncertainties. The computationally derived $\Delta_f H^\circ_{298}$ values suggest that the experimental results for seven compounds may be in error by as much as 10−30 kJ/mol. Especially large difference between calculated and experimental values was found for $P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$. Experimental data for these molecule are incorrect and should be remeasured. It may be proposed that, until new accurate measurements resolve the available discrepancies with experiment, the enthalpies of formation obtained in this work provide a consistent set of reliable estimates for thermodynamic modeling the processes involving phosphorus(III) containing species.

Overall, a reasonable estimate of the error of theoretical enthalpies of formation obtained in this work from the G3X atomization energies is ±10 kJ/mol. Even better accuracy may be achieved by using the isodesmic reactions. We have illustrated the importance of well-balanced isodesmic reactions for determining accurate enthalpies of formation, especially at lower levels of theory.

A large variety of GAVs involving the phosphorus(III) atom has been derived from enthalpies of formation obtained in this work. A set of 45 consistent GAVs significantly extends the applicability of Benson's group additivity method and may be used to estimate the enthalpies of formation of larger organophosphorus(III) compounds, where high level quantum chemical calculations are impracticable.

Acknowledgment. This research was supported by the Russian Foundation for Basic Research under Grant No. 05-03-32069.

Supporting Information Available: B3LYP/6-31G(d,p) electronic energies, symmetry and rotational constants for the most stable conformers of 55 organophosphorus(III) compounds, Table 1S. Experimental enthalpies of formation of gaseous atoms at 0 K and thermal corrections for elements in their standard states used in enthalpy of formation calculations, Table 2S. Enthalpies of formation, G3X, G3XMP2, and B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) electronic energies, zero-point energies, and thermal corrections for species considered in this work, Table 3S. This material is available free of charge via the Internet at http://pubs.acs.org.

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