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Benson Group Additivity Values of Phosphines and Phosphine Oxides: Fast and Accurate Computational Thermochemistry of Organophosphorus Species

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ABSTRACT

Composite quantum chemical methods W1X-1 and CBS-QB3 are used to calculate the gas phase standard enthalpy of formation, entropy and heat capacity of 38 phosphines and phosphine oxides for which reliable experimental thermochemical information is limited or simply nonexistent. For alkyl phosphines and phosphine oxides, the W1X-1 and CBS-QB3 results are mutually consistent and in excellent agreement with available G3X values and empirical data. In the case of aryl-substituted species, different computational methods show more variation, with G3X enthalpies being furthest from experimental values. The calculated thermochemical data are subsequently used to determine Benson group additivity contributions for 24 Benson groups and group pairs involving phosphorus, thereby allowing fast and accurate estimations of thermochemical data of many organophosphorus compounds of any complexity. Such data are indispensable, for example, in chemical process design or estimating potential hazards of new chemical compounds.

Introduction

Even though organophosphorus compounds have become more and more important in chemical processes and applications, empirical data of their thermochemical properties remain scarce.[1] This is in part due to the fact that many phosphorus compounds are toxic, pyrophoric or otherwise highly reactive,[2, 3, 4] which causes practical difficulties in preparing and handling them. In addition, accurate calorimetric determination of basic thermochemical properties of phosphorus (and other) compounds necessitates careful control over their combustion processes and ability to analyze all products, neither of which is trivial. It is therefore not surprising that many older thermochemical reference values have been shown to be unreliable or erroneous. For example, incorrect standard enthalpies of formation of some orthophosphates have been given in the National Bureau of Standards (NBS) tables,[5, 6] and data using red, not white, phosphorus as the elemental reference has not always been corrected for modern standards.[7, 8]

Considering the challenges associated with the experimental determination of thermochemical properties of phosphorus (and other) compounds, composite quantum chemical methods have gained ground as an important alternative.[9] The W1 approach was the first widely applicable protocol to reach "chemical accuracy", that is, computational results reaching the accuracy of well-performed thermochemical experiments, 4 kJ mol^{-1}.[10] The main limitation of the W1 method is that it is restricted to systems with roughly 10 heavy atoms, though recent improvements, such as the W1-F12 and W1X-n procedures, have increased the barrier to around 20 heavy atoms while retaining the accuracy of the original W1 approach.[11, 12] Even more accurate composite methods have also been introduced, such as W3/W4, FPD and HEAT,[13–16] but their

application is limited to all but the smallest systems. For molecules with 20 to 30 heavy atoms, the use of G-*n*- and CBS-*x*-based protocols is in the majority of cases feasible,[17–24] though not all of their variants are able to reach chemical accuracy. The accuracy can be improved, however, if the values given by G-*n* and CBS-*x* protocols are combined for statistical gain,[25] but this naturally also increases the associated computational cost.

It was proposed already in the early 20th century that the properties of larger chemical species could be estimated by dividing them into fragments whose contributions to the calculated property remain virtually constant from one species to another.[26] One of the most successful applications of this approach in the context of thermochemical properties is the group additivity method published by Benson and Buss,[27] and later extended to liquid and solid phases by Domalski and Hearing.[28, 29] For organic compounds, Benson group additivity method is an extremely powerful tool as it can be used to estimate thermochemical properties with near chemical accuracy, provided that the underlying data are of sufficient quality. Over the years, several revisions to Benson's work, such as that of Cohen's,[30] have been published and the method has also been completely reformulated, for example, by Salmon and Dalmazzione.[31] Nevertheless, Benson's original work remains the cornerstone for many recent improvements in the field.[32, 33]

One of the most significant advantages of Benson group additivity method is its speed: thermochemical properties can be accurately estimated within a fraction of a second, irrespective of the size of the system in question. This can be contrasted with high-level composite quantum chemical methods that require significantly more CPU-time, from days to weeks, along with specialized software and hardware. Consequently, it has been of interest to extend Benson group additivity method beyond organic systems (that is, molecules containing atoms other than C, H, N, O, S and halogens), with organophosphorus compounds making no exception. For larger molecules, this

is nowadays considered the best available alternative to obtain thermochemical properties with near chemical accuracy.[34] The approach has in the past been used in the context of phosphorus compounds by Glaude *et al.*[35, 36] and Dorofeeva and Moiseeva,[37–39] who have reported values for roughly a hundred phosphorus-based Benson groups.

The purpose of the current work is threefold. First, even though the existing list of phosphorus-based Benson groups is extensive, it is by no means exhaustive. In fact, there are some very common groups whose thermochemical contributions, if known, would allow the application of Benson's methodology to estimate the thermochemical properties of many organophosphorus compounds, such as alkyl and aryl phosphines, for which the current thermochemical data are based on rudimentary estimates.[40] Second, the works of Glaude *et al.* and Dorofeeva and Moiseeva have utilized the CBS-QB3 and G3X methods.[41–43] In this respect, it would be of interest to determine if W1-based approaches would lead to any significant changes in the derived group contributions, thereby providing an important reference point for evaluating the accuracy of the published data. Third, the group contributions reported by Dorofeeva and Moiseeva are not fully compatible with Benson's original work or with the work of Glaude *et al.*, because Cohen's revised data sets were used in deriving them. For this reason, the existing data values cannot be easily implemented in thermochemical software based on Benson's formulation. This is not insignificant as enthalpy estimators, such as the ASTM Computer Program for Chemical Thermodynamics and Energy Release Evaluation (CHETAH),[44] are widely used in assessing hazards related to instabilities of chemical compounds or in chemical process design.

Computational Methods

Calculations were performed for phosphines (**a**) and phosphine oxides (**b**) with alkyl (**1–12**) and aryl (**13–19**) substituents shown in Chart 1 using composite methods W1X-1[12] and CBS-QB3.[41]

The CBS-QB3 method was used as implemented in the *Gaussian* program package[45] to obtain composite electronic energies, E_e(CBS-QB3), via an automated procedure. In contrast, W1X-1 electronic energies, E_e(W1X-1), were obtained by manually combining results from eight single point energy calculations performed with the *Molpro* code,[46, 47] namely HF-CABS/cc-pVDZ-F12,[48–52] HF-CABS/cc-pVTZ-F12, CCSD-F12b/cc-pVDZ-F12,[53, 54] CCSD-F12b/cc-pVTZ-F12, CCSD(T)/aug'-cc-pV(D+d)Z,[55–58] CCSD(T)/aug'-cc-pV(T+d)Z, FC-MP2/cc-pCVTZ[58, 60] and DKH-MP2/cc-pCVTZ.[61, 62]

	R₁	R₂	R₃
1	H	H	H
2	Me	H	H
3	Me	Me	H
4	Me	Me	Me
5	Et	H	H
6	Et	Et	H
7	Et	Et	Et
8	Et	Me	Me
9	Pr	H	H
10	ⁱPr	H	H
11	ˢBu	H	H
12	ᵗBu	H	H
13	Ph	H	H
14	Ph	Ph	H
15	Ph	Ph	Ph
16	Ph	Me	H
17	Ph	Me	Me
18	Ph	Ph	Me
19	Ph	Et	Me

Chart 1.

In the W1X-1 method, the HF-CABS energy and the CCSD and (T) energy components, ΔCCSD and Δ(T), were first each extrapolated to the complete basis set (CBS) limit by using the extrapolation formula $E_L = E_{CBS} + AL^{-\alpha}$,[63] where L is the cardinal number of the basis set (2 or 3) and α is an adjustable parameter (5, 3.6725 and 2.0436 for HF-CABS, ΔCCSD and Δ(T), respectively).[12] Second, a combined core correlation and scalar-relativistic correction term, Δ(C+R), was calculated as the difference between the frozen-core MP2/cc-pCVTZ and all-electron Douglas-Kroll-Hess MP2/cc-pCVTZ electronic energies. Finally, the composite electronic energy E_e (W1X-1) was obtained as the combined sum of the four aforementioned terms, E_{CBS}(HF-CABS), E_{CBS}(ΔCCSD), E_{CBS}(Δ(T)) and E(Δ(C+R)).

For both W1X-1 and CBS-QB3 methods, the underlying geometry optimizations and frequency calculations were performed with the B3LYP[64–67] density functional in combination with cc-pV(T+d)Z and 6-311G(2d,d,p) basis sets,[23, 24, 57, 58] respectively. Conformational scans were performed for molecules with multiple low-lying conformers at the B3LYP/6-311G(2d,d,p) level of theory to locate the lowest energy geometry with respect to this functional-basis set combination. These conformers were also used in the W1X-1 calculations without performing new conformational scans at the more expensive B3LYP/cc-pV(T+d)Z level of theory. Scale factors of 0.985 (W1X-1) and 0.990 (CBS-QB3) were applied in the evaluation of gas phase thermochemical data, that is, internal thermal enthalpy, heat capacity and entropy, at 298.15 K. In calculation of entropy and heat capacity terms, the rigid rotor-harmonic oscillator approximation was used. However, to account for the effect of internal rotations, rotation modes involving single bonds were treated as hindered rotors using the procedure implemented in *Gaussian*. Periodicity 3 and symmetry number 3 were used for rotations involving methyl groups, while the corresponding values for alkyl and phenyl groups were 3 and 1, and 2 and 2, respectively.

Standard gas phase enthalpies of formation, $\Delta_f H°$, were obtained with the help of atomization energy approach in which reference values for enthalpies of formation of gaseous atoms and thermal corrections for elements in their standard states were taken from tables published by the Committee on

Data of the International Council for Science (CODATA).[68]

The organophosphorus compounds discussed in this work were partitioned into Benson groups to derive new group contributions for standard gas phase enthalpy of formation, $\Delta_f H°$ (W1X-1 and CBS-QB3), entropy, $S°$ (B3LYP/cc-pVTZ+d) and heat capacity, $C_p°$ (B3LYP/cc-pVTZ+d). Optimization of group contributions was accomplished by means of the generalized reduced gradient non-linear least squares fitting algorithm,[69] which used the calculated thermochemical data and reference values for carbon-based groups as input.[27–29] The resulting set of values were found to be unique within 1–2 kJ mol^{-1} or J K^{-1} mol^{-1}, as confirmed by multiple optimization runs employing different sets of initial values.

All Benson groups involving a methyl group bonded to a heteroatom were assigned the same contribution since, by definition, the value for methyl group does not change (except for the physical state) no matter to what it is attached.[27] In calculation of Benson enthalpy contributions, the methyl repulsion corrections of Domalski and Hearing were used for tertiary (–2.26 kJ mol^{-1}) and quaternary (–4.56 kJ mol^{-1}) carbon atoms, whereas the calculation of entropy contributions utilized appropriate corrections for optical isomerism ($R \ln n$, where n is the total number of stereoisomers; 2 for **11**, **16** and **19**) as well as internal (σ_{int}) and external (σ_{ext}) symmetries ($-R \ln \sigma_{tot}$, where $\sigma_{tot} = \sigma_{ext}\prod^i (\sigma_{int})_i$; 2 for **13**, 3 for **2**, **5** and **9**, 4 for **14**, 6 for **16** and **19**, 9 for **3**, **6**, **10** and **11**, 12 for **18**, 18 for **17**; 24 for **15**; 27 for **8**; 81 for **4**, **7** and **12**).[28, 29]

Results and Discussion

W1X-1 and CBS-QB3 Thermochemical Data

Thermochemical data were calculated for 38 phosphines and phosphine oxides shown in Chart 1 with composite methods W1X-1 and CBS-QB3. The compounds considered include one to three alkyl and/or aryl substituents, each containing one to six carbon atoms. It needs to be noted that, due to the limits posed by the

available computational resources and high-speed disk space in particular, triphenyl-substituted phosphine and phosphine oxide could only be treated at the CBS-QB3 level. The calculations for diphenyl species were also prohibitively expensive with the W1X-1 method, requiring nearly 2.5 TB of fast disk space and several days of wall-clock time, while the same jobs could be run in hours at the CBS-QB3 level.

A literature search for thermochemical data of organophosphorus compounds yielded standard enthalpies of formation for more than a dozen simple phosphines and phosphine oxides related to this work. However, a critical review of the original reports revealed that many of these values were in fact, either partially of fully, based on theoretical estimates such as the Franklin's group equivalence method,[70] or derived using ionization potentials that had error estimates in the order of tens of kJ mol^{-1}.[71] Thus, only nine values of enthalpies of formation were left that could be considered both empirical and accurate enough to be useful for evaluating the performance of the chosen computational methods to calculate standard enthalpies of formation of phosphines and phosphine oxides.[72–77]

Table 1 reports W1X-1 and CBS-QB3 thermochemical data for the 19 alkyl and aryl phosphines considered in this work; CBS-QB3 entropies and heat capacities have been omitted as they are nearly identical with the W1X-1 data. Experimental values and G3X results reported by Dorofeeva and Moiseeva have been included in Table 1 for comparison purposes (where available).[37–39, 72–76]

It can be immediately seen that for alkyl phosphines **1a**–**12a**, the W1X-1 and CBS-QB3 methods yield standard enthalpies of formation that differ, on average, only by less than 4 kJ mol^{-1}. The G3X results are, in general, slightly closer to W1X-1 than CBS-QB3, though in most cases all three methods yield values within 4 kJ mol^{-1} from each other. The same is true when the different computational methods are compared with empirical data, and all three methods are, in general, able to reach experimental accuracy within 3σ.

Table 1. Calculated and experimental standard (298 K) enthalpies of formation ($\Delta_f H°$, kJ mol^{-1}), entropies ($S°$, J K^{-1} mol^{-1}) and heat capacities ($C_p°$, J K^{-1} mol^{-1}) of alkyl and aryl phosphines.

Molecule	$\Delta_f H°$				$S°$	$C_p°$	$C_p°$(500 K)	$C_p°$(1000 K)
	W1X-1	CBS-QB3	G3X[37–39]	Exptl.[72–76]	W1X-1	W1X-1	W1X-1	W1X-1
1a (PH$_3$)	9.7	1.8	10.3	5.4 ± 1.7	210.1	28.7	38.0	55.7
2a (PH$_2$Me)	−17.7	−22.3	−15.8	−14.1 ± 8.0	260.0	49.2	70.5	104.6
3a (PHMe$_2$)	−55.5	−57.0	−52.9		297.8	74.1	105.6	154.4
4a (PMe$_3$)	−102.7	−101.6	−99.9	−97.0 ± 4.6	321.7	102.3	143.2	205.2
5a (PH$_2$Et)	−37.4	−40.0	−34.9	−36.5 ± 1.5	292.8	71.6	104.9	155.9
6a (PHEt$_2$)	−89.5	−87.4		−89.6 ± 2.1	368.4	117.0	171.0	255.1
7a (PEt$_3$)	−151.9	−146.0	−149.5	−152.7 ± 2.8	427.8	166.2	240.1	355.5
8a (PMe$_2$Et)	−119.5	−116.7			365.9	124.1	175.6	255.2
9a (PH$_2$Pr)	−60.6	−61.2	−57.4		327.6	93.8	138.4	206.6
10a (PH$_2$^{i}Pr)	−62.1	−63.3	−59.9		322.9	95.6	140.9	208.1
11a (PH$_2$^{i}Bu)	−82.3	−81.6			356.3	117.9	174.4	258.6
12a (PH$_2$^{t}Bu)	−93.6	−94.4	−93.0		347.8	121.5	179.7	262.2
13a (PH$_2$Ph)	123.0	124.5	125.7		343.4	101.9	163.5	243.0
14a (PHPh$_2$)	222.6	231.5			460.5	181.7	294.4	432.5
15a (PPh$_3$)	-	325.5	336.0	320.2 ± 4.7	559.1	268.4	430.5	627.1
16a (PHMePh)	84.3	87.9			371.1	129.6	204.3	296.4
17a (PMe$_2$Ph)	39.4	45.5			400.1	156.7	242.3	349.9
18a (PMePh$_2$)	177.4	187.6			466.0	210.0	336.2	493.5
19a (PMeEtPh)	19.5	27.2			445.5	180.3	271.8	394.8

The computational results for the parent phosphine, PH$_3$, stand out from the rest in Table 1. The difference between W1X-1 and CBS-QB3 enthalpies is surprisingly large, as much as 7.9 kJ mol^{-1}. Interestingly, the combustion calorimetry derived standard enthalpy of formation of PH$_3$ is 5.4 ± 1.7 kJ mol^{-1},[72] and, therefore, exactly in between the two computational results. The other experimental value reported for the parent phosphine, 11.8 ± 8 kJ mol^{-1},[73] has been obtained via database mining and is associated with such large uncertainty that it cannot be used to evaluate the relative performance of W1X-1 and CBS-QB3 any further. While the G3X result for PH$_3$ is closer to W1X-1, a very high-level CCSD(T)/CBS study by Hawort and Bacskay gave a standard enthalpy of formation of 3.8 kJ mol^{-1},[78] in seemingly better agreement with the CBS-QB3 data. Possible reasons for the varying performance of different computational methods in predicting the standard enthalpy of formation of PH$_3$ are discussed in more detail in context of the corresponding oxide, OPH$_3$.

Before discussing the results for aryl-substituted species, the calculated heats of formation for alkyl phosphines can be compared with the simple estimates currently reported in the literature.[40] This shows that the published values are, in fact, reasonable for the simplest of systems such as trimethylphosphine (−93.7 kJ mol^{-1}) and ethylphosphine (−44.0 kJ mol^{-1}) but become inferior for more complicated species like diethylphosphine (−112.2 kJ mol^{-1}) and propylphosphine (−78.6 kJ mol^{-1}).

For aryl phosphines **13a**–**19a**, the data in Table 1 show that the differences between W1X-1 and CBS-QB3 standard enthalpies of formation are greater than for alkyl-substituted species, on average more than 6 kJ mol^{-1}. It is also evident that the W1X-1 values are systematically slightly less endothermic than the CBS-QB3 values, whereas no such obvious trend was seen in the case of alkyl phosphines. Due to the scarcity of both G3X results and experimental data, very few conclusions can be made about the relative and absolute performance of different theoretical approaches for aryl phosphines. However, it can be pointed out that the empirical standard enthalpy of formation of triphenylphosphine, 320.2 ± 4.7 kJ mol^{-1},[76] is well reproduced by the CBS-QB3 method, while the result given by the G3X approach, 336 kJ mol^{-1}, [37–39] is not even within 3σ of the experimental value.

Table 2. Calculated and experimental standard (298 K) enthalpies of formation ($\Delta_f H°$, kJ mol^{-1}), entropies ($S°$, J K^{-1} mol^{-1}) and heat capacities ($C_p°$, J K^{-1} mol^{-1}) of alkyl and aryl phosphine oxides.

Molecule	$\Delta_f H°$				$S°$	$C_p°$	$C_p°$(500 K)	$C_p°$(1000 K)
	W1X-1	CBS-QB3	G3X[37–39, 78]	Exptl.[76, 77]	W1X-1	W1X-1	W1X-1	W1X-1
1b (OPH$_3$)	−204.6	−217.5	−203.3		233.8	34.0	51.0	76.6
2b (OPH$_2$Me)	−277.0	−285.0			278.6	58.6	88.	130.4
3b (OPHMe$_2$)	−348.1	−352.0			313.2	85.4	126.0	184.7
4b (OPMe$_3$)	−417.4	−418.6	−416.7	−431.0 ± 8.0	343.4	114.2	158.8	226.3
5b (OPH$_2$Et)	−294.1	−300.0			316.4	80.6	118.5	176.4
6b (OPHEt$_2$)	−383.3	−384.1			383.4	129.8	190.3	280.7
7b (OPEt$_3$)	−466.4	−464.0			438.0	180.9	262.2	382.4
8b (OPMe$_2$Et)	−434.0	−433.8			383.1	135.6	193.0	279.8
9b (OPH$_2$Pr)	−316.9	−320.8			344.9	102.0	155.5	231.8
10b (OPH$_2^i$Pr)	−321.2	−325.7			345.3	106.3	155.6	228.6
11b (OPH$_2^i$Bu)	−341.4	−344.1			376.1	126.7	189.2	282.0
12b (OPH$_2^t$Bu)	−354.0	−358.2			368.7	132.6	195.3	282.9
13b (OPH$_2$Ph)	−130.5	−132.2			360.6	113.8	182.8	269.7
14b (OPHPh$_2$)	−57.7	−51.0			472.6	195.5	314.7	462.8
15b (OPPh$_3$)	-	25.1	26.0	2.8 ± 7.0	568.5	281.9	449.1	649.1
16b (OPHMePh)	−203.3	−202.2			385.2	141.1	221.0	321.1
17b (OPMe$_2$Ph)	−274.2	−270.4			411.7	168.1	258.0	373.3
18b (OPMePh$_2$)	−128.4	−120.5			483.2	224.1	353.4	514.6
19b (OPMeEtPh)	−293.7	−289.1			454.3	192.5	291.6	421.0

Literature data of standard entropies and heat capacities were only found for the parent phosphine, methyl phosphine and triphenyl phosphine.[73, 79] As expected, the results obtained with the W1X-1 method, that is, at the B3LYP/cc-pVTZ+d level, given in Table 1, are in good agreement with the reference values. For example, the calculated entropy of the parent phosphine is 210.1 J K^{-1} mol^{-1}, which is spot on with the value reported in NIST-JANAF Thermochemical Tables, 210.2 J K^{-1} mol^{-1}.[79] Furthermore, Active Thermochemical Tables (ATcT) give 257.5 and 56.0 J K^{-1} mol^{-1} for the standard entropy and heat capacity of methyl phosphine,[73] respectively, while the corresponding W1X-1 values are 260.0 and 49.2 J K^{-1} mol^{-1}. In similar fashion, the literature values of standard entropy and heat capacity of triphenylphosphine are 557.4 and 267.9 J K^{-1} mol^{-1},[73] respectively, in good agreement with the calculated values of 559.1 and 268.4 J K^{-1} mol^{-1}.

Table 2 reports W1X-1 and CBS-QB3 thermochemical data for the 19 alkyl and aryl phosphine oxides **1b–19b** considered in this work; experimental values and data calculated by Dorofeeva and Moiseeva and Haworth and Bacskay with the G3X method have been included for comparison (where available).[37–39, 76-78] It is clear that no statistical analysis of the performance of different computational methods can be made, because only two empirical standard enthalpies of formation are available and they are both associated with relatively large uncertainties. As the data from G3X calculations are equally limited, the numbers in Table 2 only allow a comparison between the W1X-1 and CBS-QB3 methods. This shows that, in general, W1X-1 predicts the standard enthalpies of formation of alkyl phosphine oxides slightly less exothermic than CBS-QB3, whereas the opposite is true for aryl-substituted species. However, in both cases the two sets of values differ, on average, only by 4 kJ mol^{-1}.

The results in Table 2 also show that the different computational methods yield highly differing values for the standard enthalpy of formation of the simplest phosphine oxide, OPH$_3$. The CBS-QB3 enthalpy is 12.9 kJ mol^{-1} more exothermic than the W1X-1 value, while the G3X method gives an enthalpy very close to W1X-1. For comparison, the CCSD(T)/CBS result, −215.5 kJ mol^{-1},[78] is in better agreement with the CBS-QB3 value than with either W1X-1 or G3X. Thus, the behavior of different

computational methods mirrors exactly that seen in the case of the parent phosphine. Of all the different theoretical values available, the CCSD(T)/CBS data are the most trustworthy. Based on the analysis published by Haworth and Bacskay,[78] the differences between CCSD(T)/CBS and W1X-1 or G3X results for PH_3 and OPH_3 can be attributed to incomplete treatment of core-valence correlation within the latter two computational methods, which, when combined with the atomization approach, can lead to significant errors even in the case of chemically simple molecules.[80] In this context, the surprisingly good performance of CBS-QB3 most likely originates from fortuitous error cancellation as the method has the most rudimentary treatment of core-valence correlation and lacks scalar-relativistic corrections altogether.[41, 42]

The performance of W1X-1, CBS-QB3 and G3X methods in prediction of standard enthalpies of formation has previously been evaluated with respect to the G3/99 (W1X-1 and G3X, mean absolute deviations of 3.7 and 3.7 kJ mol^{-1} against 222 reference values)[12, 43] and G2/97 (G3X and CBS-QB3, mean absolute deviations of 3.6 and 4.5 kJ mol^{-1} against 148 reference values)[41–43] data sets, which, however, contain relatively few phosphorus compounds. The results in Tables 1 and 2 show that, with the exception of the parent species PH_3 and OPH_3 and their triphenyl-substituted analogues, the different composite methods show remarkably comparable performance. Thus, even though W1X-1 is theoretically the most advanced and robust composite method considered herein, both CBS-QB3 and G3X perform equally well in the majority of cases and are able to do so with significantly smaller computational cost.

Benson Thermochemical Group Contributions

The primary aim of this work was to use the calculated thermochemical data in Tables 1 and 2 to derive Benson group contributions for common phosphorus-based groups as this would allow the easy and accurate estimation of thermochemical properties of many organophosphorus compounds, be they simple or complex.

Table 3 gives the W1X-1 and CBS-QB3 derived thermochemical Benson group contributions involving alkyl phosphines and phosphine oxides, that is, for the groups $C-(H)_2(C)(P)$, $C-(H)(C)_2(P)$, $C-(C)_3(P)$, $P-(H)_2(C)$, $P-(H)(C)_2$, $P-(C)_3$, $C-(H)_2(C)(PO)$, $C-(H)(C)_2(PO)$, $C-(C)_3(PO)$, $PO-(H)_2(C)$, $PO-(H)(C)_2$ and $PO-(C)_3$. The respective G3X enthalpy values, reported by Dorofeeva and Moiseeva, have been included for comparison (where available).[37–39] However, as noted earlier, a direct comparison between the results is not fully justified as the latter are based on Cohen's,[30] not Benson's,[27] work, and use, for example, a slightly different reference enthalpy value for the methyl group. It should also be noted that all group contributions in Table 3, including the ones published earlier, have been rounded to the nearest integer, a convention adopted by Holmes and Aubry,[32, 33] as any better precision cannot simply be justified. This also emphasizes the internal character of Benson's approach to estimate, not to calculate, thermochemical parameters.

The results in Table 3 show that the W1X-1 and CBS-QB3 derived group contributions to enthalpy differ, on average, by 4 kJ mol^{-1}. This parallels the behavior seen in the case of standard enthalpies of formation and further underlines the comparable performance of W1X-1 and CBS-QB3 in extending Benson's methodology towards phosphorus-based groups. A comparison between present work and prior G3X data also shows only minor differences, despite the fact that the group contributions are calculated from different reference values. However, the G3X results for the group $C-(C)_3(P)$ in Table 3 appear somewhat anomalous. Even though the difference between W1X-1 and G3X enthalpies, 8 kJ mol^{-1}, could be attributed to the use of different reference values, the large deviations in entropy and heat capacity, 130 and 33 J K^{-1} mol^{-1},[37–39] respectively, are not as easily explained.

Table 3. Thermochemical Benson group contributions for standard (298 K) enthalpies of formation ($\Delta_f H°$, kJ mol^{-1}), entropies ($S°$, J K^{-1} mol^{-1}) and heat capacities ($C_p°$, J K^{-1} mol^{-1}) derived from computational data.

Group	$\Delta_f H°$			$S°$	$C_p°$	$C_p°$(500 K)	$C_p°$(1000 K)
	W1X-1	CBS-QB3	G3X[37–39]	W1X-1	W1X-1	W1X-1	W1X-1
C-(H)$_2$(C)(P)	−18	−15	−17	35	22	33	50
C-(H)(C)$_2$(P)	3	8	1	−59	20	30	41
C-(C)$_3$(P)	24	29	32	−137	21	30	34
P-(H)$_2$(C)	23	17	23	139	23	32	43
P-(H)(C)$_2$	32	28	29	61	22	27	31
P-(C)$_3$	25	25	25	−24	25	25	20
C-(H)$_2$(C)(PO)	−17	−15	−19	34	22	34	49
C-(H)(C)$_2$(PO)	2	6	8	−59	21	28	37
C-(C)$_3$(PO)	21	25		−137	23	29	29
PO-(H)$_2$(C)	−235	−243		160	33	48	69
PO-(H)(C)$_2$	−264	−268		78	34	46	60
PO-(C)$_3$	−290	−292		−6	37	42	45

Interestingly, the only species investigated by Dorofeeva and Moiseeva containing the group C-(C)$_3$(P) is tert-butylphosphine for which the G3X standard entropy is reported to be 347.6 J K^{-1} mol^{-1} and, hence, very close to the W1X-1 value of 343.2 J K^{-1} mol^{-1}. This strongly suggests that the G3X group contributions for C-(C)$_3$(P) were incorrectly derived from otherwise appropriately calculated data. In agreement with this explanation, the standard entropy of tert-butylphosphine becomes 519 J K^{-1} mol^{-1} when estimated using the published G3X group contributions for C-(P)(C)$_3$, C-(C)(H)$_3$ and P-(C)(H)$_2$ (−7, 127 and 145 J K^{-1} mol^{-1}, respectively),[37–39] which would imply the presence of an unreasonably negative symmetry correction of −171 J K^{-1} mol^{-1}.

Benson's work includes enthalpy group contributions for four groups given in Table 3, namely C-(H)$_2$(C)(P) (−10 kJ mol^{-1}), C-(H)$_2$(C)(PO) (−14 kJ mol^{-1}), P-(C)$_3$ (29 kJ mol^{-1}) and PO-(C)$_3$ (−305 kJ mol^{-1}).[81] However, the standard enthalpies of formation used to derive the group contributions for C-(H)$_2$(C)(P) and C-(H)$_2$(C)(PO) were from Hartley et al. and, hence, from a compilation that is not entirely empirical.[82] Thus, a comparison between computationally and experimentally derived group contributions is justified only in the case of P-(C)$_3$ and PO-(C)$_3$. While the match is perfect for P-(C)$_3$, the difference between computational and empirical values is notable for PO-(C)$_3$, as much as 15 kJ mol^{-1}. Because both W1X-1 and CBS-QB3 gave very similar group contributions for PO-(C)$_3$, the large difference between the computational and experimentally derived values can be assigned to significant uncertainties in the empirical standard enthalpies of formation of relevant compounds. For example, the literature value for trimethylphosphine oxide is −431.0 ± 8.0 kJ mol^{-1},[77] that is, approximately 10–15 kJ mol^{-1} more exothermic than any of the three calculated values given in Table 2. Consequently, redetermination of the experimental standard enthalpy of formation of trimethylphosphine oxide is clearly needed and the experimental value should, most likely, be adjusted upwards. The same holds also for triphenylphosphine oxide, in which case the adjustment is, however, to the opposite direction.

Out of the wealth of data on phosphorus-based Benson groups reported by Glaude et al.,[35, 36] only two groups, C-(H)$_2$(C)(PO) and P(O)-C$_3$, are common with the current study. The CBS-QB3 enthalpy, entropy and heat capacity contributions reported by Glaude et al. are, in respective order, −17 kJ mol^{-1}, 37 J K^{-1} mol^{-1} and 21 J K^{-1} mol^{-1} for C-(H)$_2$(C)(PO), and −289 kJ mol^{-1}, −8 J K^{-1} mol^{-1} and 48 J K^{-1} mol for P(O)-C$_3$, in excellent agreement with the data in Table 3. While this might seem trivial at first, after all, the same composite method was used in both studies, it is less so when taking into account that completely different sets of reference compounds were employed to derive the group contributions.

Table 4. Thermochemical Benson group pair contributions for standard (298 K) enthalpies of formation ($\Delta_f H°$, kJ mol^{-1}), entropies ($S°$, J K^{-1} mol^{-1}) and heat capacities ($C_p°$, J K^{-1} mol^{-1}) derived from computational data.

Group pair	$\Delta_f H°$			$S°$	$C_p°$	$C_p°$(500 K)	$C_p°$(1000 K)
	W1X-1	CBS-QB3	G3X[37-39]	W1X-1	W1X-1	W1X-1	W1X-1
P-(H)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(P)	54	55	56	108	34	49	67
P-(H)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(P)	85	93		−6	46	66	81
P-(C$_B$)3 + 3 C$_B$-(C$_B$)$_2$(P)	-	118	128	−46	64	88	99
P-(C)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(P)	54	59		−70	38	48	48
P-(C)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(P)	82	92		−124	48	69	80
P-(H)(C)(C$_B$) + C$_B$-(C$_B$)$_2$(P)	58	61		11	36	51	59
PO-(H)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	−200	−201		125	46	69	94
PO-(H)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(PO)	−196	−189		1	59	86	111
PO-(C$_B$)3 + 3 C$_B$-(C$_B$)$_2$(PO)	-	−182	−172	−132	74	107	121
PO-(C)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	−260	−257		−59	50	65	73
PO-(C)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(PO)	−224	−216		−107	62	86	101
PO-(H)(C)(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	−230	−229		26	47	68	83

Table 4 gives the W1X-1 and CBS-QB3 derived thermochemical Benson group contributions involving aryl phosphines and phosphine oxides. In this case, the different Benson groups always occur in pairs, which makes it impossible to derive individual group contributions in any unambiguous way. As discussed earlier by Ashcraft and Green,[83] the situation can be handled in two ways: either one publishes the data for different pairs of Benson groups, as original done by Benson, or one assigns an arbitrary reference value to one (or many) of the group(s), which can then be used to derive individual contributions for all others. In the current work, the first of the two aforementioned approaches was chosen, despite the fact that some authors, like Kirklin and Domalski,[76] and later Benson,[81] have reported individual group contributions based on preset reference values.

The results in Table 4 show that the W1X-1 and CBS-QB3 derived group pair contributions to enthalpy differ, on average, by 5 kJ mol^{-1}, in good agreement with the performance of the two methods in predicting the standard formation enthalpies of aryl-substituted phosphines and phosphine oxides. The enthalpy values in Table 4 can be compared with the G3X data published by Dorofeeva and Moiseeva (where available). [37-39] Enthalpy contributions of 53, 119 and −181 kJ mol^{-1} have been reported for groups P-(H$_2$)(C$_B$), P-(C$_B$)$_3$ and PO-(C$_B$)$_3$, respectively, which, together with the contribution of 3 kJ mol^{-1} for the groups C$_B$-

(C$_B$)$_2$(P) and C$_B$-(C$_B$)$_2$(PO), lead to the G3X values listed in Table 4. It is apparent that the G3X and CBS-QB3 results differ greatlly for pairs involving groups P-(C$_B$)$_3$ and PO-(C$_B$)$_3$, which originates from differences in the calculated standard formation enthalpies of triphenylphosphine and the corresponding oxide with these methods. In this context, Kirklin and Domalski have reported experimentally derived Benson group contributions for the relevant groups,[76] leading to group pair contributions of 113 and −205 kJ mol^{-1} for P-(C$_B$)$_3$ + 3 C$_B$-(C$_B$)$_2$(P) and PO-(C$_B$)$_3$ + 3 C$_B$-(C$_B$)$_2$(PO), respectively. Both of these values are in better agreement with the CBS-QB3 data than with G3X, supporting the view that the G3X method is the least accurate of the three when it comes to predicting thermochemical parameters of aryl-substituted phosphines and phosphine oxides.

To illustrate the usefulness of the derived group contributions, the standard enthalpy of formation of triethylphosphine was estimated using the values reported in Table 3 and compared with the reported empirical value of −152.7 ± 2.8 kJ mol^{-1}.[75] Even though triethylphosphine was used in the analysis of different computational methods, the enthalpies, entropies and heat capacities reported in Table 1 were excluded from the data set when deriving group contributions given in Table 3.

Triethylphosphine contains three different Benson groups, C-(C)(H)$_3$, C-(H)$_2$(C)(P) and P-

(C)$_3$, of which the first two appear with a factor of 3. The corresponding enthalpy contributions are −42,[27–29] −18 (W1X-1) and 25 kJ mol^{-1} (W1X-1), yielding a standard enthalpy of formation of −155 kJ mol^{-1}, in excellent agreement with both experimental and calculated values. If the analysis is performed using group contributions obtained with the CBS-QB3 method, the estimated enthalpy of formation of triethylphosphine is more inferior, −146 kJ mol^{-1}.

As another example of the applicability of the derived Benson group contributions, they can be used to test the validity of older thermochemical work. A value of −464.0 ± 28.0 kJ mol^{-1} has been reported for the standard enthalpy of formation of tributylphosphine oxide in the solid state.[84] Tributylphosphine oxide contains four different Benson groups, PO-(C)$_3$, C-(H)$_2$(C)(PO), C-(H)$_2$(C)$_2$ and C-(H)$_3$, of which the last three appear with factors 3, 6 and 3, respectively. The corresponding enthalpy contributions are −290 (W1X-1), −17 (W1X-1), −21 and −42 kJ mol^{-1},[27–29] yielding a standard gas phase enthalpy of formation of −593 kJ mol^{-1}; the value obtained with the CBS-QB3 group contributions is almost identical, −589 kJ mol^{-1}. These results uniformly indicate that the empirical standard enthalpy of formation of tributylphosphine oxide must be in error as the gas phase enthalpy is more exothermic than the solid state measurement, while the opposite should hold. As already discussed in the literature,[85] the experimental calorimetric study of tributylphosphine oxide has multiple possible sources of error, most notably the use of a static, not rotating, bomb and subsequent incomplete combustion of the compounds in question.

In order to further verify the accuracy of the present estimation, the standard gas phase enthalpy of formation of tributylphosphine oxide was calculated with the W1X-1 and CBS-QB3 methods. In this case, a full conformational scan was impossible to perform at the B3LYP/6-311G(2d,d,p) level of theory as the rotation of all single bonds within the butyl chains leads to 3^9 = 19683 conformers, of which not all are,

however, unique. Consequently, we chose two lowest energy conformers found for tripropylphoshpine oxide as our targets: a C_3 symmetric propeller-like structure and a T-shaped C_s symmetric conformer. CBS-QB3 calculations performed for the two aforementioned conformers gave enthalpies of −587.5 and −588.4 kJ mol^{-1}, respectively, in excellent agreement with the estimated value. The W1X-1 method could only be applied to investigate the C_s symmetric conformer (non-Abelian point group symmetry cannot be utilized in *Molpro*), for which a slightly more exothermic standard gas phase enthalpy of formation of −602.9 kJ mol^{-1} was obtained.

Conclusions

In this work, we used composite quantum chemical methods W1X-1 and CBS-QB3 to calculate thermochemical data for 38 alkyl- and aryl-substituted phosphines and phosphine oxides, and applied these values to derive group contributions for 24 Benson groups or group pairs, many of which had not been determined before.

The calculated W1X-1 and CBS-QB3 standard gas phase enthalpies of formation were, for the most part, in good agreement with each other and earlier G3X results. Biggest differences were observed for the parent phosphine and phosphine oxide, which require the use of very high-level methods to be modelled accurately. Significant variations, that is, enthalpy differences greater than 4 kJ mol^{-1}, were also seen in computational data for aryl-substituted species, in which case W1X-1 predicts the most exothermic enthalpies, followed by CBS-QB3 and G3X.

The scarcity of empirical data makes straightforward comparisons between calculated and experimental results challenging. However, taking into account the overall performance of W1X-1 and CBS-QB3 in predicting standard gas phase enthalpies of formation, both methods are able to compete with experimental, calorimetric, approaches that are typically associated with large

uncertainties. While W1X-1 is the most accurate composite method employed, its use over CBS-QB3 (or G3X) is not well-justified for most phosphines and phosphine oxides due to the relatively minor improvement in performance associated with significantly higher computational cost. In fact, the molecules investigated in the current contribution are among the biggest systems treated with the W1X-1 method (up to 15 heavy atoms within C_1 point group), thus, establishing a valuable benchmark for future studies.

The calculated thermochemical data were used to derive group or group pair contributions of standard gas phase enthalpy of formation, entropy and heat capacity for various Benson groups. The data are uniform and fully compatible with the original work in the field, thus, permitting the use of the reported values "as is" in many software for fast and accurate computational thermochemistry. The group contributions derived from W1X-1 and CBS-QB3 enthalpies were, for the most part, not significantly different, which arises from statistical gain resulting from the use of more than one compound for the derivation of any particular group contribution. In the case of alkyl-substituted species, the prior G3X group contributions were found to be comparable with the new W1X-1 and CBS-QB3 values, whereas significant differences between the three methods were observed for aryl phosphines and phosphine oxides.

Most importantly, the current study showed that the derived Benson group contributions can be used to accurately estimate standard gas phase enthalpies of formation of organophosphorus compounds. The estimates are of chemical accuracy, as shown for triethylphosphine, and can, therefore, be used to validate or disprove prior experimental data, as shown for tributylphosphine oxide. Hence, in light of the results presented herein, a valuable objective for future studies is the use of composite quantum chemical methods to extend Benson's methodology to compounds containing other heteroatoms such as boron and silicon. Efforts towards these objectives are currently in progress and will be reported in due course.

Acknowledgments

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