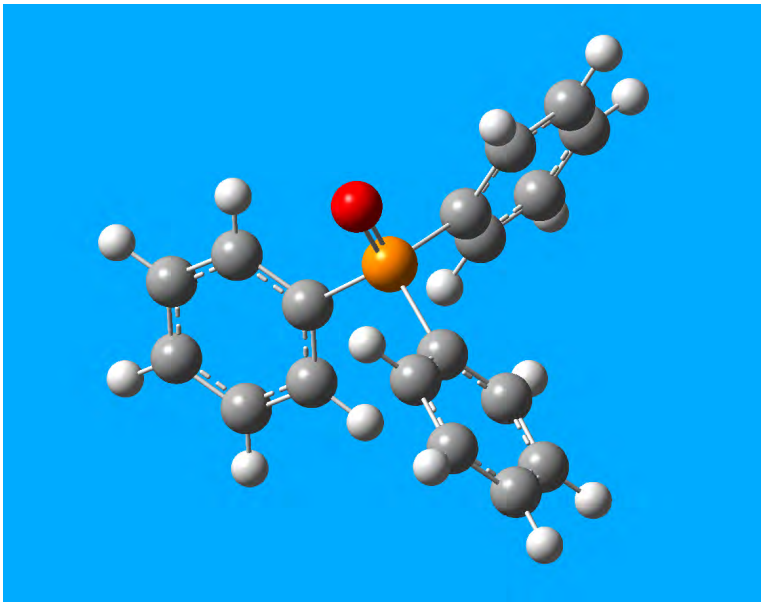
JYU DISSERTATIONS 581

Hannu Vuori

Extending Benson Group Increment Theory to Compounds of Phosphorus, Silicon, and Boron with Computational Chemistry



UNIVERSITY OF JYVÄSKYLÄ
FACULTY OF MATHEMATICS
AND SCIENCE

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ABSTRACT

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Extending Benson Group Increment Theory to Compounds of Phosphorus, Silicon, and Boron with Computational Chemistry
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A huge gap exists between the 200 million+ known chemical species listed in the Chemical Abstracts Service Registry and the few thousand compounds with data available in thermodynamic databases. In this work, high-level quantum chemical composite methods were applied to calculate thermodynamic properties for more than 300 compounds of phosphorus, silicon, and boron with little or no experimental data available. The acquired standard gas-phase enthalpies of formation, entropies, and heat capacities were compared to and contrasted with results from prior computational investigations as well as experimental studies. This revealed inconsistencies, outliers, and even systematic errors in the experimental data, with revised values suggested for thermodynamic properties of many fundamental small molecules. The data also enabled the derivation of new and updated group contribution values for almost 150 phosphorus-, silicon-, and boron-based groups within the framework of the Domalski-Hearing version of the Benson Group Increment Theory. These new values allow the thermodynamic properties of both existing and new chemical species of the three elements in question to be estimated quickly and inexpensively compared to the time and resources required if similar tasks were performed with quantum chemical methods of equal accuracy. Such advances in predictive methodology are highly valuable in many areas of chemical research and industry.

Keywords: quantum chemistry, composite methods, Benson Group Increment Theory, chemical thermodynamics, thermochemistry, enthalpy of formation, entropy, heat capacity, phosphorus, silicon, boron

TIIVISTELMÄ (ABSTRACT IN FINNISH)

Vuori, Hannu
Bensonin ryhmäkontribuutiomenetelmän laajentaminen fosforin, piin ja boorin yhdisteisiin laskennallisen kemian menetelmien avulla
Jyväskylä: Jyväskylän yliopisto, 2022, 59 s. + alkuperäiset artikkelit
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Chemical Abstract Service on kemiallisten yhdisteiden tunnistenumerotietokanta, josta löytyy nykyään yli 200 miljoonaa tietuetta. Monien yhdisteiden ominaisuuksista ei kuitenkaan tiedetä paljoa ja esimerkiksi yhdisteiden termodynaamisia ominaisuuksia listaavissa taulukoissa on tyypillisesti vain muutamia tuhansia rivejä. Tässä työssä määritettiin tarkkojen kvanttikemiallisten yhdistelmämenetelmien avulla yli 300 fosforin, piin ja boorin yhdisteen termodynaamiset ominaisuudet, kuten niiden muodostumisentalpia, entropia ja ominaislämpökapasiteetti kaasufaasissa ja standarditilassa. Saatuja tuloksia verrattiin kokeelliseen dataan sekä aiempien laskennallisten tutkimusten tuloksiin. Tällä tavalla voitin osoittaa kokeellisesta datasta löytyvän runsaasti epäjohdonmukaisuuksia sekä myös karkeita ja systemaattisia virheitä. Monissa tapauksissa tutkimuksen tuottamat arvot yhdisteiden termodynaamisille ominaisuuksille ovat kokeellisia arvoja huomattavasti tarkempia, mikä puoltaa työn tulosten käyttämistä jatkosovelluksissa. Työssä määritettiin myös uudet ja päivitetyt Bensonin ryhmäkontribuutiot lähes 150:lle fosforin, piin ja boorin Bensonin ryhmälle käyttäen Domalskin ja Hearingin versiota Bensonin menetelmästä. Määritettyjen ryhmäkontribuutioiden avulla on mahdollista arvioida niin olemassa olevien kuin uusien kemiallisten yhdisteiden termodynaamisia ominaisuuksia nopeasti ja hyvällä tarkkuudella, mitä voidaan hyödyntää esimerkiksi monilla teollisuuden ja tutkimuksen aloilla.

Avainsanoja: kvanttikemia, yhdistelmämenetelmät, Bensonin ryhmäkontribuutiomenetelmä, kemiallinen termodynamiikka, termokemia, muodostumisentalpia, entropia, ominaislämpökapasiteetti, fosfori, pii, boori

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FOREWORD

At schoolboy age, I happened to read a fascinating parable stating that the size of a human being is about the geometric mean between the sizes of a hydrogen atom and the Sun. As long as I can remember, I have been interested in all observable phenomena in nature, including both the smallest and the largest of objects. Not so much in people, but mainly in astronomical, biological, and technical objects, especially electrical ones. In short: science. I learnt to read at the age of five and had read every science and nature-related book found at home before starting school. My father was a goldsmith and needed some applied chemistry in his daily work, which explains the fact that we had some books at home from which I could learn elementary chemistry and physics. I even tried simple experiments with rudimentary equipment.

As a child, I often dreamed of a profession where I could do research and find out how everything works. For decades I had to wait for the opportune moment, but this certainly developed my patience. I passed my Matriculation Exam at Jyväskylä Lyceum in 1967 and began chemistry studies at the University of Jyväskylä the following year. For financial reasons, I had to postpone my graduate studies and began working as a teacher in mathematics, physics, and chemistry at elementary schools in various municipalities. Neither I nor my pupils have many glorious memories from this period. Teaching simply is not a profession where my personal characteristics excel. During this time, I was fortunately able to complete all degree requirements and graduated with a M. Sc. degree in 1982.

I had worked on electronics as a hobby since the age of twelve, starting my projects with electron valves and continuing with transistors and integrated circuits as soon as they became available and fit to my limited budget. In 1978, I had the opportunity to build a microcomputer based on a construction kit. The only way to get it to do something useful involved writing a machine code in raw hexadecimal notation. As I saw my first program work as planned, my immediate thought was "Yessss! This looks like something I could do for a living!". The thought became reality in 1984 and from that point onwards I often imagined of writing a computer application that would be useful to chemists. Unfortunately, it was not possible to pursue this path while working for companies like Olivetti, Nokia, or Tieto, which together took over twenty years of my life.

The starting point of the current project can be traced back to the year 1994, when I decided to continue with doctoral studies. The very moment occurred when Professor Matti Lindström at LUT University opened his desk drawer and dug out a couple of sheets from a thick pile of papers. They contained a sketch of specifications describing a computer program capable of calculating fundamental thermodynamic properties based on an unspecified group increment theory. These sheets of A4 size papers were literally his answer to my question, whether Professor Lindström would have a suitable topic for doctoral research. The interview altogether lasted a few minutes.

It later turned out that the sheets of paper originated from Outokumpu Research Center where Dr. (Tech.) Antti Roine was responsible of software development. I contacted Antti directly and immediately started planning the code with LUT University providing me access to experimental thermodynamic data. In the following months, I created a crude and limited but albeit a working demo of the program as a standalone application. I had the possibility to demonstrate it at Outokumpu Research Center and at LUT University, but soon after I was recruited to Nokia Telecommunications as a Senior Software Engineer and the project went idle. Nevertheless, these two gentlemen deserve my most humble thanks for directing me towards the light at the end of a tunnel and my dream of doing research.

Next time I could consider doing research and continuing doctoral studies was after my retirement from Tieto Oyj were I held the post of a Senior Software Designer until 2010. As time had passed, Outokumpu Research Center had become Outotec, which was later merged with Metso Minerals to become Metso Outotec. Nevertheless, some things had not changed, and Antti was still responsible for software development at Outotec. When I asked him if a group increment theory-based software component was still needed, he confirmed that such module is still missing from their flagship software HSC Chemistry and a person capable of writing it had not yet shown up. After a short conversation, a deal was made.

Because both the programming environment and the required software tools had changed during the decades I was occupied elsewhere, I started my work from scratch. After an intense learning, planning, coding, testing, and debugging period, the first version of Benson estimation module went to customer use in 2014. At Outotec, M. Sc. (Tech.) Lauri Mäenpää was mainly responsible of testing the software and he made valuable suggestions for improvements to the user interface and the available features. My job was to do all the code planning and writing, including database build-up. Around that timeframe, I also contacted my original *alma mater*, the University of Jyväskylä, for a possibility to enroll in doctoral studies. I was immediately accepted to the program with a study plan revolving around computational methods, thermodynamic properties, and Benson group contributions.

At this point, I want to thank my supervisors Prof. Emer. Erkki Kolehmainen and Prof. Heikki M. Tuononen. Without my old friend Erkki's continuous encouragement, experience, wide contact network, and unshaken trust in my ability to succeed in this project, I probably would have given up at some stage. Without Heikki's professional skills, insight, knowledge, and vision, combined with the talent of teaching, I would never have gotten results out of the heavy computing tasks in decent amount of time or been able to write such an interesting narrative. Special thanks also go to Dr. J. Mikko Rautiainen for his timely advice and tireless sharpness in checking endless columns of numbers that I produced. I also wish to thank all members of our research group for treating me like a peer and clearly accepting a more seasoned member to their younger party. Among them I want to name Assistant Prof. Jani Moilanen, who has

always been available and ready to help. The University of Jyväskylä and the Academy of Finland (Grant Number 324680 to H.M.T.) are gratefully acknowledged for financial support.

Last but not least, my warm thanks go to my wife, Anna-Liisa, for her loving care during our nearly 54 years of marriage and her unselfish toil to support my efforts. Warm thanks also go to my whole family. Many of my friends have encouraged and appreciated my work and deserve a special notion. Among them, I am very grateful to M. Sc. (Tech) Kauko Manner who gave me valuable guidance in solving mathematical problems.

I have thoroughly enjoyed the opportunity to return to learning and studying chemistry with tools that were not imaginable when I first started my studies more than five decades ago. Unfortunately, I will not be around for the third time to see what this branch of science looks like after another half a century has gone by…

Jyväskylä 14.10.2022
Hannu Vuori

"And further, by these, my son, be admonished:
of making many books there is no end;
and much study is a weariness of the flesh."

(Eccl. 12:12)

LIST OF INCLUDED PUBLICATIONS

(I) Vuori, H. T.; Rautiainen, J. M.; Kolehmainen, E. T.; Tuononen, H. M. Benson Group Additivity Values of Phosphines and Phosphine Oxides: Fast and Accurate Computational Thermochemistry of Organophosphorus Species. *Journal of Computational Chemistry* **2019**, *40*, 572–580.

(II) Vuori, H. T.; Rautiainen, J. M.; Kolehmainen, E. T.; Tuononen, H. M. High-Level *ab Initio* Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches. *Journal of Physical Chemistry A* **2022**, *126*, 1729–1742.

(III) Vuori, H. T.; Rautiainen, J. M.; Kolehmainen, E. T.; Tuononen, H. M. Computational thermochemistry: extension of Benson group additivity approach to organoboron compounds and reliable predictions of their thermochemical properties. *Dalton Transactions* **2022**, *51*, 15816–15829.

(IV) Vuori, H. T.; Rautiainen, J. M.; Kolehmainen, E. T.; Tuononen, H. M. Correction/Addition to "High-Level ab Initio Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches". *Journal of Physical Chemistry A* **2022**, *126*, 5873–5879.

Author's contribution

The author brought under consideration the original project idea of widening the application area of Benson Group Increment Theory by using thermodynamic properties calculated with computational chemistry. He chose the compounds to be included in the study, performed the quantum chemical calculations, prepared the spreadsheets for data post-processing, searched the chemical literature for relevant reference material, and wrote the initial drafts of all prepared publications.

FIGURES

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1 INTRODUCTION

One of the most widely discussed subjects today is energy: its price, sources, and consumption, as well as the consequences of its production and usage.[1] At the heart of this debate are the availability, cost, safety, and environmental impact of different energy sources, and questions pertaining to the production, storage, transport, and environmental issues of the energy being produced and used. Whenever any forms of combustion are considered as energy sources or material waste is generated in energy production or consumption, chemistry inevitably plays a major role in solving any of the emerging problems.[2,3] News about alternative energy sources and new means to utilize them, as well as making efficient and sustainable use of the existing ones, are seen in the headlines virtually every day. At the center of this development is, again, chemistry, paving the way for fields such as hydrogen technology and mitigating the effects of climate change by improving carbon capture and storage systems.[4,5] Even fusion energy, while primarily a part of nuclear physics research, needs chemists to provide, for example, new materials suitable for the extreme conditions present in the reactor environment.[6,7] The temporal variability of wind and solar energy necessitates the use of storage systems to provide a continuous flow of electricity, which, once again, calls for chemists to come up with new battery technologies suitable for the task.[8] Simply put, chemistry is omnipresent in the energy sector, contributing to sustainable energy harnessing and improving the efficiency of energy generation, transmission, and use.

Whether the focus is on using chemical compounds as energy sources or as reactants in the chemical industry, where vast amounts of raw materials are converted into valuable products every day, the efficient use of resources requires knowledge and understanding of chemical thermodynamics, the study of heat and work associated with chemical reactions or physical phase changes.[9,10] For example, the enthalpy of combustion specifies the energy released as heat when a compound, such as a fuel, undergoes complete combustion, whereas the Gibbs free energy sets the theoretical upper limit for work that may be performed by the same reaction. It goes without saying that not a single chemical process can be scaled to the level of mass production

without conducting detailed mass and energy balance analyses, underlining the importance of thermodynamics in chemical engineering.[11] Even though chemical thermodynamics has existed as a field of science for nearly two centuries and its importance is widely recognized, the pace of its development has had a hard time keeping up with that of synthetic chemists. Specifically, the Chemical Abstracts Service (CAS) Registry assigns a number for every chemical substance described in scientific literature, and the current count has just passed the 200 million mark.[12] Of these, experimental thermodynamic data are readily available for only thousands,[13,14] leaving the thermochemistry of most known compounds completely in the dark. While there are well-established experimental methods to obtain new data, their practical application is in many cases both laborious and time-consuming, typically raising the costs associated with such measurements to a high or even very high level for all but the simplest chemical species.[15] Such a situation has made it necessary to explore alternative means to obtain accurate thermodynamic data, and computational methods have gradually been put to the fore, finally reaching a maturity and a level to give predictions that match the accuracy of state-of-the-art experiments.[16]

1.1 Aims of the study

The goal of this work was three-pronged. First, as explained in the introduction, there is a clear need for accurate thermodynamic data for many different chemical species. In the current work, the focus was on compounds of phosphorus, silicon, and boron because these are all in their own way problematic for experimental calorimetry. Consequently, the avenue followed herein made use of modern high-level composite quantum chemical methods to arrive at consistent and accurate standard gas-phase enthalpies of formation, entropies, and specific heat capacities for more than 300 target species.

Second, the results of high-level calculations were compared to existing experimental data, which allowed the identification of important trends, possible outliers, and systematic errors. Furthermore, detailed assessment of the results in light of data from prior computational investigations gave insight on the performance of different composite methods in predicting the thermodynamic properties of compounds of phosphorous, silicon, and boron.

Third, the computational results were used as a basis to derive and optimize group additivity contributions for almost 150 phosphorus-, silicon-, and boron-based groups within the framework of Benson Group Increment Theory. These allow the estimation of thermodynamic properties for a wide variety of compounds of the three aforementioned elements with unprecedented accuracy *vs.* speed ratio. Such data are indispensable, for example, in modern chemical engineering and heat balance calculations in particular.

2 CHEMICAL THERMODYNAMICS

2.1 Heat and fundamental thermodynamic properties

Thermochemistry is the study of thermal, or heat, energy, associated with chemical reactions or physical phase changes such as melting and boiling.[9–11] Excluding nuclear energy, matter typically contains energy in two forms: as thermal energy, which is essentially kinetic energy that results from the movement of the smallest particles of the matter, and as chemical energy, which can be viewed as an expression of potential energy stored in chemical bonds. Chemical reactions convert chemical energy to other forms such as thermal energy, electrical energy, radiant energy, or even mechanical energy. Matter can also have mechanical energy caused by its macroscopic state of motion or due to its position relative to a zero potential.

Because heat energy can be detected and observed by human senses without any technological means, it has interested people since prehistoric times. The true nature of thermal energy was under study and debate for millennia, with historical records dating back to ancient Greek philosophers.[17] The first obstacle on the way to understanding the real character of thermal energy was the difficulty in making a distinction between intensity and quantity of heat energy, that is, the temperature and the amount of thermal energy. One classic example of this is the thermoscope built by Philo of Byzantium during the 3rd century BC. It was clearly an early version of a thermometer, but no one recognized it or understood its possible use.[18]

The first clues to the physical reality of heat energy and the essence of its properties started to emerge in the early 19th century.[19,20] An obstacle on this path to understanding was the ancient misconception that heat energy is a form of matter, which seemed logical at the time when thinking of, for example, thermal expansion.[21,22] If heat energy were a kind of matter, a material body into which heat flows needs more space and must therefore expand. The explanation

seemed good enough to rationalize heat transfer by convection and conduction. More puzzling, however, was the ability of heat energy to move by radiation without mediating matter, which fit to no known material. The long-lasting and incorrect explanation for this phenomenon was the universe-filling fictive substance called *aether*, introduced by Aristotle as the element of stars.[23] The concept of *aether* propagated through ancient and medieval times up to the last decades of the 19th century, when it was believed to fill the whole universe. The killing stroke to *aether* theory, albeit a slow one, was provided by the Michelson–Morley experiment and its failure to detect any significant difference between the speed of light in the direction of Earth's motion and the speed of light at right angles to it.[24] At this point in history, the Maxwell equations had already been published,[25] and it was soon realized that through space, the transfer of thermal energy involves radiation, and thermal radiation is simply electromagnetic radiation emitted by all matter at non-zero temperatures.

The fundamental laws of thermodynamics are the origin of all other rules and equations discussed in this Chapter and are, therefore, briefly listed here in one of their many forms:[26]

0th law:	If systems A and B are in thermodynamic equilibrium with each other and so are systems B and C, then A and C must also be in equilibrium.
1st law:	The total energy of an isolated system is constant; energy can be neither created nor destroyed, only transformed from one form to another.
2nd law:	The entropy of an isolated system can only stay constant or increase.
3rd law:	Any thermodynamic process cannot reach the temperature of absolute zero by a finite number of steps and within a finite time.

The numbering of the laws may appear odd, but the explanation is logical. The 1st, 2nd, and 3rd laws were first established in the 19th century, while the 0th law was introduced by Ralph Fowler as late as in the 1930s. The already established numbering scheme was preserved because it was so widely used and well-known at the time, and the new law simply became the 0th law. It is put first on the list because it essentially defines temperature and is, therefore, relevant to all the other laws.

A direct consequence of the 2nd law of thermodynamics is that heat never spontaneously flows from a lower temperature reservoir to a higher temperature one between initially noncorrelated systems, or to be precise, this has never been observed as the law is empirical. This is also the cause of the 3rd law because nothing can be colder than absolute zero, so there is no way to remove the last remnant of heat energy, which always keeps the temperature of an object at a finite value. As a curiosity, the 2nd law of thermodynamics puts thermal energy into a unique position in nature in that all other energy forms can be completely transformed into it but never *vice versa*.

Among all thermodynamic properties of matter, there are three fundamental ones that are most relevant to the current work and will be briefly discussed herein: molar heat capacity C, molar entropy S, and molar enthalpy H. To further elaborate on these, the concept of the thermodynamic state of a system is needed. This is defined by the initial condition of the system at a given time that is identifiable by values of a suitable set of parameters known as state variables. Once these variables have been set, the values of all thermodynamical properties of the system become uniquely determined. In many cases, the thermodynamic state is chosen so that it is in thermodynamic equilibrium.

Molar heat capacity, molar entropy, and molar enthalpy are state functions of the system, which relate several state variables that depend on the equilibrium thermodynamic state of the system and not on the path taken to reach it. Molar entropy and heat capacity are commonly expressed in SI units as joule per mole kelvin ($J \cdot mol^{-1} \cdot K^{-1}$), while molar enthalpy typically uses the unit kilojoule per mole ($kJ \cdot mol^{-1}$). Common to all these three properties is that none of them can be directly measured with any instrument.

In the following, the thermodynamic concepts of heat capacity, entropy, and enthalpy are briefly introduced. For a more detailed account on the topic, the reader should consult almost any university-level textbook in physical chemistry, which is precisely where most of the following discussion has been adapted from.[27]

2.2 Heat capacity *C*

Of the three fundamental thermodynamic properties discussed above, perhaps the simplest to understand and determine is heat capacity C. It was also the first one of the three to be named and formulated in its current meaning by Joseph Black in the 1750s. Black was also the first person to clearly distinguish between heat and temperature.[28]

Simply stated, heat capacity is a physical property of matter that denotes the amount of heat energy to be supplied to an object to produce a one kelvin change in its temperature. It is therefore a measure of the ability of the system to absorb thermal energy without undergoing a large change in temperature. If this quantity is given per unit of mass of the substance, one obtains specific heat capacity, whereas if it is given per one mole of the substance, one arrives at molar heat capacity (similar arguments apply to entropy and enthalpy). Thus, heat capacity (like entropy and enthalpy) is an extensive property and depends on the actual physical object in question, whereas specific heat capacity and molar heat capacity are intensive properties. As heat capacity varies with pressure P and temperature T, and thereby with the phase of the substance, it is sometimes written in the form $C(P,T)$.

The introduction of heat energy into a substance not only raises its temperature but usually causes an increase in its volume and/or pressure, depending on whether the system is confined or not. Thus, a distinction between

heat capacities in constant pressure C_P (isobaric) and in constant volume C_V (isochoric) need to be made. The condition of constant pressure means that the substance is allowed to expand during heating, which is equivalent to doing mechanical work against external pressure, and that work must come from the heat energy provided. If the volume is kept constant, no work can be done and the heat energy that would have gone into doing it must instead contribute to the internal energy of the system, thereby further raising its temperature. This leads to significantly higher numeric values for C_P than C_V, especially when the substance in question is a gas.

Molar heat capacity can be defined as the derivative of the energy of the system with respect to the temperature under the specified conditions of either constant pressure or constant volume:

$$C_\mathrm{P} = \left(\frac{\partial H}{\partial T}\right)_\mathrm{P} \text{ and} \tag{I}$$

$$C_\mathrm{V} = \left(\frac{\partial U}{\partial T}\right)_\mathrm{V}, \tag{II}$$

where U is the internal energy of the system and H is its enthalpy. One implication of these equivalences is that molar heat capacity is a state variable, just like internal energy and enthalpy are, and Hess's law (see below) can be applied to molar heat capacities as it is applied to other state variables.

Equation I can be used to derive Kirchhoff's law in thermochemistry, which relates the enthalpy change for a reaction at two different temperatures T_1 and T_2 to the integrated change in molar heat capacity between those temperatures

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_\mathrm{P}\, \mathrm{d}T. \tag{III}$$

If the temperature range from T_1 to T_2 is very small, Equation III allows the experimental determination of C_P from enthalpy changes at constant pressure.

2.3 Entropy *S*

The initial theoretical concept of entropy S was already anticipated by Sadi Carnot in 1824, but its current form was presented and named in 1865 by Rudolf Clausius, one of the most influential characters of modern thermodynamics.[29,30] As a concept, entropy is given very diverse meanings in different branches of science, but here it is understood and discussed solely as a thermodynamic property.

The original definition of entropy was given by Clausius, and it relates the entropy change ΔS of a reversible process to heat exchange:

$$\Delta S = \int \frac{dQ}{T}, \tag{IV}$$

where dQ is the amount of heat transferred to the system or out of it (as indicated by its sign) and T is the absolute temperature. If the system is isolated, the heat transferred is zero by definition and the entropy of the system remains constant as $\Delta S = 0$. If, however, the process is irreversible and the system is isolated, one obtains $\Delta S > 0$, showing that entropy increases. Thus, every isolated system will proceed through chemical reactions and physical phenomena until it reaches an equilibrium state in which no macroscopic energy transfer happens, and heat is evenly distributed. This corresponds to entropy increasing until it reaches its maximum value. And no matter what kind of process proceeds in an isolated system, entropy can never decrease, allowing the 2nd law of thermodynamics to be written

$$\Delta S \geq 0 \qquad \text{(V)}$$

for any change in an isolated system and where the equality holds for a reversible process. Thus, the Clausius form of the 2nd law of thermodynamics states that in an isolated system, a spontaneous process always proceeds in the direction of increasing entropy and thermodynamic entropy can be viewed as a measure of thermal energy per unit temperature that is unavailable to do work. For a system that is not isolated, Equation V becomes

$$\Delta S \geq \int \frac{dQ}{T}. \qquad \text{(VI)}$$

The statistical definition of entropy was developed in the 1870s by Ludwig Boltzmann for an ideal gas, and it was shown to be equivalent with thermodynamic entropy to within a constant factor, nowadays known as the Boltzmann constant k_B.[31] In statistical mechanics, entropy is defined as

$$S = k_B \, ln \, W, \qquad \text{(VII)}$$

where W is the number of microstates compatible with a given macrostate, with all microstates treated equally with even weights. Thus, entropy increases with the number of energetically equivalent ways to arrange the components of the system to achieve a particular macrostate. In other words, the state with the highest entropy has the greatest dispersal of energy. As spontaneous processes proceed in the direction of increasing entropy, spontaneous processes are those that result in greater dispersal or randomization of energy.

Entropy and heat capacity are related by the following expressions:

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P \text{ and} \qquad \text{(VIII)}$$

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V. \qquad \text{(IX)}$$

Thus, entropy changes can be obtained by integration of C_P/T values from the lowest temperature of measurement to the reported temperature at constant pressure:

$$\Delta S = \int \frac{C_P dT}{T}. \quad \text{(X)}$$

A distinct feature of entropy that differentiates it from, for example, enthalpy, is its natural zero level: entropy of a perfect crystal of a pure substance at 0 K would be exactly zero, as implied by Equation VII with the number of microstates W being only one. This is in fact how the 3rd law of thermodynamics is formulated in some instances.

2.4 Enthalpy H

The last of the three fundamental thermodynamic properties discussed herein is enthalpy, which was conceived by Willard Gibbs in 1875, but its current name was taken into use only many years later by Heike Onnes.[32] Enthalpy was earlier called the heat content of a system, and Gibbs himself used the expression heat function for constant pressure.

Enthalpy H of a thermodynamic system is defined as the sum of its internal energy U and the product of its pressure and volume:

$$H = U + PV. \quad \text{(XI)}$$

As all three are functions of state of the system, enthalpy is also a state function. Enthalpy is typically expressed as the change in enthalpy for a process between two states at constant pressure:

$$\Delta H = \Delta U + P\Delta V. \quad \text{(XII)}$$

If only pressure-volume work is allowed, Equation XII becomes

$$\Delta H = Q_P, \quad \text{(XIII)}$$

where Q_P is the heat for the process at constant pressure. Thus, at constant pressure, the change in enthalpy represents the heat given off or used by the process. Even though ΔU is a measure of all energy, both heat and work, exchanged by the system with its surroundings and ΔH is a measure of only heat, the two quantities are often nearly identical. The change in volume is negligible for many chemical processes, save for those involving very large amounts of gas.

If for a chemical reaction $\Delta H < 0$, the reaction is said to be exothermic, meaning that it releases heat, whereas if $\Delta H > 0$, the reaction is said to be endothermic, meaning that it absorbs heat from its surroundings. Note that enthalpies and enthalpy changes for reactions vary as a function of temperature, as shown earlier by Equation III, which introduced a connection between enthalpy and heat capacity. A connection between enthalpy and entropy can be obtained by introducing the concept of Gibbs (free) energy G:

$$G = H - TS, \quad \text{(XIV)}$$

with the change in Gibbs energy defined as

$$\Delta G = \Delta H - T\Delta S, \tag{XV}$$

at constant temperature. The importance of Gibbs energy stems from the fact that it gives a single measure for spontaneity. If for a chemical reaction $\Delta G < 0$, the reaction is spontaneous, whereas if $\Delta G > 0$, the reaction is nonspontaneous. An important note to make is that a spontaneous reaction is simply a reaction that favors the formation of products at the stated conditions. In other words, spontaneity tells nothing about the rate of the reaction. It can be remarkably fast, incredibly slow, or anything in between.

Having arrived at the important connections between heat capacity, enthalpy, and entropy, one additional concept particularly relevant to the current work needs to be introduced. The standard enthalpy of formation ΔH_f° of a chemical species corresponds to the enthalpy change in a hypothetical process in which the species in question is formed directly from its constituting elements, all in their reference states, under standard conditions (typically 1 atm or 1 bar and 298.15 K; these definitions for standard conditions often apply to molar entropy and heat capacity). Consequently, all elements in their standard states have $\Delta H_f^\circ = 0$ as there is no enthalpy change involved in their formation.

Given the above definition, standard enthalpies of formation are not determined experimentally but rather calculated from other enthalpy data. A law published in 1840 by Germain Hess, nowadays known as Hess's law of constant heat summation,[33] relates the enthalpy change of a chemical reaction ΔH_r° to the standard enthalpies of formation of the products and reactants:

$$\Delta H_r^\circ = \sum_p v_p \Delta H_f^\circ - \sum_r v_r \Delta H_f^\circ, \tag{XVI}$$

where v_p and v_r are stoichiometric coefficients of products and reactants, respectively.

Hess's law is merely a manifestation of the fact that enthalpy is a state function. It allows unknown enthalpies of formation to be determined indirectly by experimentally determining the enthalpy change of an appropriate chemical reaction so that only one unknown remains in Equation XVI. This allows the determination of standard enthalpies of formation even for unstable reaction intermediates or otherwise highly reactive species that could not be studied experimentally.

If standard enthalpies of formation are available for a wide variety of compounds, the enthalpy change of any given reaction involving those species can be conveniently calculated using Hess's law. This allows, for example, the determination of the reaction equilibrium constant using the Van't Hoff equation:

$$\ln K_{eq} = -\frac{\Delta H_r^\circ}{RT} + \frac{\Delta S_r^\circ}{R}, \tag{XVII}$$

where K_{eq} is the reaction equilibrium constant, provided that the associated standard entropy change for the reaction ΔS_r° is known. Alternatively, if K_{eq} and

ΔH_r° have been determined experimentally, the standard entropy change can be easily derived. An important point to note is how the equilibrium constant depends logarithmically on the reaction enthalpy. What this means in practice is that if ΔH_r° changes by only a few $kJ \cdot mol^{-1}$, K_{eq} changes significantly more, and the reaction yield can easily decrease (or increase) by tens of %-units. This has a dramatic effect on the feasibility of any planned manufacturing process, for which reason the values of ΔH_f° used in the calculation of ΔH_r° must be as accurate as possible.

Even though the rates of chemical reactions do not directly depend on ΔH_r°, they do depend on the reaction conditions, and temperature in particular, which, in turn, is affected by ΔH_r°, unless the heat produced by the reaction (if any) is effectively dissipated away to keep the reaction rate under strict control. This is yet another reason why accurate values of ΔH_r° and ΔH_f° are essential in chemical engineering and process design. Underestimating this elementary principle and allowing sloppy design or working practices has caused far too many disasters in the history of the chemical industry.[34]

3 CALORIMETRY

Calorimetry is the science of measuring changes in state variables of a system for deriving, for example, heat capacities or enthalpy and entropy changes associated with chemical reactions.[15] Some of the fundamental concepts of calorimetry are briefly described herein to pay tribute to one of the key methods that is used to determine enthalpies of formation experimentally, often through the determination of enthalpies of combustion with bomb calorimetry.

3.1 Basics of calorimetry

The simplest calorimetric experiments involve determining heat capacities and enthalpy changes related to phase changes. The sheer idea of measuring the amount of heat energy released or bound in physical or chemical phenomena was initially presented by Joseph Black in 1756 when experimenting with his idea of latent heat in phase transitions.[35] The first experiments were conducted five years later and involved simple phase changes known to everyone: melting of ice and boiling of water. The earliest practical application of calorimetry was an ice calorimeter, which uses the heat energy absorbed by the melting ice to determine heat capacities of liquids and solids or enthalpies of simple chemical reactions. The use of an ice calorimeter was first documented by Antoine Lavoisier and Pierre-Simon Laplace in the early 1780s.[18] They used the apparatus to prove that the respiratory gas exchange of all living animals results from one kind of combustion. Lavoisier also coined the name for the instrument by combining the Greek and Latin words for heat and measuring.[36]

Perhaps the simplest calorimeter that can be used to measure either enthalpy changes of physical or chemical processes or heat capacities of insoluble solids consists of an insulated vessel containing a known liquid, usually water, and equipped with both a thermometer and a mechanical stirrer.[15] Most readers of this work are probably familiar with this kind of experiment by having tried it themselves in physics class in high school or university, using nothing fancier

than one thivck styrofoam coffee cup (or two nested ones) equipped with a lid as the calorimetric vessel (Figure 1). A typical measurement for determining the heat capacity of an unknown solid sample, such as a metal, starts with recording the temperature of the water inside the cup. Then the weighed specimen under study, precisely heated to a known temperature, is submerged into the water and the cup is covered with a lid. Stirring is then started and temperature change is observed by reading the thermometer display until thermal equilibrium is reached. When the masses and temperature changes involving the vessel, the water in it, and the used specimen are known, the specific heat capacity of the metal in question can be calculated.

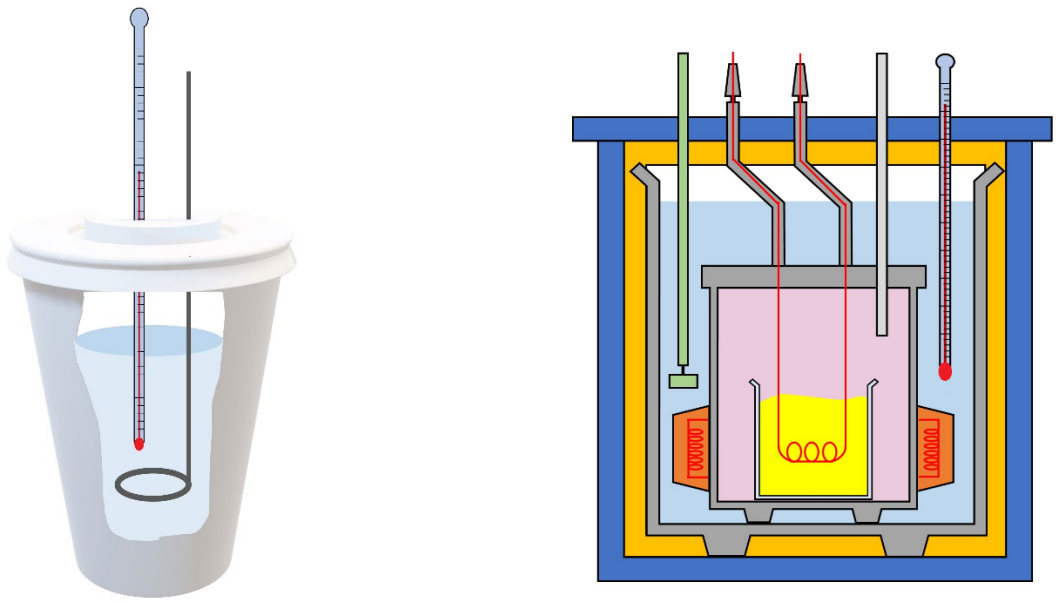


Figure 1. A simple coffee cup calorimeter with a thermometer and a stirrer (left). A schematic view of a typical bomb calorimeter (right).

3.2 Bomb calorimeter

The simple coffee cup calorimeter introduced above is an example of a constant-pressure calorimeter. Although much more sophisticated in their design, all research-grade constant-pressure calorimeters operate on the same fundamental principle as the coffee cup calorimeter and are particularly well-suited for studying reactions carried out in solution at atmospheric pressure. As can be easily imagined, if the chemical reaction to be studied involves gaseous products, such as combustion, a constant-pressure calorimeter is hardly the best choice. In such a case, a constant-volume calorimeter, also known as a bomb calorimeter, is used.[15] The first one of these was devised in the 1880s by Pierre Berthelot, who used a platinum-coated steel container to withstand the action of the gases resulting from the combustion of hydrocarbons.[37] The purpose of the platinum

lining was not to make the vessel more robust but simply to avoid corrosion errors. The name bomb calorimeter originates from the fast combustion rate caused by pressurized oxygen used in the burning process and the thick steel walls needed to keep the equipment, the bomb, intact during the reaction.

In a classical bomb calorimeter, the specimen under study is placed in a steel cup inside the steel bomb of a fixed volume (Figure 1).[38] The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion is an exothermic process, the temperature of the water bath must increase. If the heat capacity of the bomb and the mass of water are known, and the temperature changes are recorded, the heat released can be calculated. Because bomb calorimetry occurs at constant volume, the heat released corresponds to change in internal energy ΔU rather than change in enthalpy ΔH. The latter can, however, be conveniently calculated from the former by considering the amount of work done during the combustion reaction, which in the case of solid specimens is simply nRT, where n is the amount of gas produced (in moles).

Bomb calorimetry gives the enthalpy of combustion of a particular compound at given conditions. Once this is known, the enthalpy of formation of the compound can be obtained by using Hess's law, provided that the enthalpies of formation of the reaction products are known. While straightforward in principle, the practical application of bomb calorimetry is much more laborious for all but the simplest of compounds, such as common hydrocarbons, which give reliably predictable combustion products. However, there are many more elements in the periodic table besides carbon and hydrogen, and many of these present problems of their own to calorimetry.

One particularly illustrative case of problems in bomb calorimetry involves compounds of sulfur, as sulfur can be oxidized into both dioxide and trioxide during the burning process.[39] In a typical scenario, complete conversion to the trioxide could be expected in a bomb calorimeter with excess of oxygen, but incomplete combustion can nevertheless result, which renders the exact stoichiometry of the combustion reaction difficult to determine. Fortunately, this problem can be solved by introducing nitrogen into the bomb along with oxygen, leading to the formation of nitrogen oxides that catalyze the formation of sulfur trioxide. However, even though the combustion of a sulfur compound would lead solely to sulfur trioxide, the trioxide can easily react with the water formed in the bomb, generating heterogeneous deposit of sulfuric acid on the inner wall. While this side reaction can be properly accounted for in the associated thermochemical calculations, one needs to know the exact amount of the acid formed. This presents, again, a problem, because the distribution of the acid is uneven and can vary greatly in samples taken from different parts of the bomb. Fortunately, a solution to this problem exists, and it has led to the generation of a new type of instrument, a moving, or rotating, bomb calorimeter that allows efficient mixing of the reactants and formation of a perfectly defined final state.[40]

Volumes have been written about the application of bomb calorimetry to specific types of compounds, and each account typically describes problems

specific to the elements in question.[41] Most often these are related to: a) incomplete combustion, b) oxidation of the crucible or other parts of the bomb or its fittings, c) formation of acids and their subsequent reactions, d) impurities in the used oxygen and any side reactions associated with them, e) heat exchange with the environment arising from slow reaction times, and f) problems related to loading of the bomb or analysis of its contents after combustion. Even though it is not the purpose of this work to offer a complete account of calorimetry or its problems, let alone their various solutions, the above list is illustrative. It not only shows the scope of the problems but also underlines the great skill, patience, and experience that scientists in this field have demonstrated over decades of hard work in trying to solve every single one of them.

4 COMPOSITE QUANTUM CHEMICAL METHODS

Earlier it was noted that there are currently 200 million+ compounds in the CAS Registry,[12] whereas experimental thermodynamic data is available for only some thousands of them.[13,14] Furthermore, given the vast array of problems associated with determining thermochemical quantities of chemical species with calorimetry and the overall sad outlook of the field in general,[42] it is unlikely that the above ratio will move closer to 1:1 in any reasonable time frame. However, there is no reason to be dismayed, as high-level theoretical calculations and composite quantum chemical methods have finally evolved to a point where they can take, and have already taken, the place of the primary workhorse to obtain new thermodynamic data.[16] It is therefore justified that the details of some of the most common composite approaches relevant to the current work are briefly outlined. It is assumed that the reader has prior knowledge in computational chemistry because its fundamentals are far too wide to be treated herein.

4.1 Basics of composite quantum chemical methods

Composite quantum chemical methods, also known as thermochemical recipes, are theoretical procedures that aim to calculate thermodynamic properties of chemical species both accurately and fast.[16] The motivation behind composite methods is simple to understand. All thermodynamic quantities can be calculated exactly for any given system if one first obtains the exact nonrelativistic energy using the full configuration interaction method within an infinite basis set (impossible) and then augments the result with residual energetic contributions pertaining to relativity, anharmonicity, and other effects, again, calculated at the highest possible level of theory (equally impossible). Because this approach is not viable in practice, composite quantum chemical methods come to the rescue and aim to find all possible shortcuts that can be taken without compromising accuracy any more than is necessary, while ensuring that the method remains computationally feasible. In a typical scenario, one first sets the target accuracy level,

the maximum size of molecular system that the method should handle, and the time constraint, and then optimizes the composite methodology within those boundaries.

Composite quantum chemical methods have been developed starting in the late 1980s, and one of the first of its kind was the Gaussian-1 (G1) theory by John Pople and colleagues.[43] Since those times, Moore's law has ensured that the speed and capability of computers has doubled every two years,[44] leading to consistent development of more accurate composite methods that can treat ever larger systems in less time. Currently, the mainstream of composite methods, such as the G-*n* approaches and complete basis set (CBS) formulations, can easily treat systems with up to 50 heavy non-hydrogen atoms. However, they do not, in general, reach chemical accuracy, that is, mean absolute deviation (MAD) less than 4 $kJ \cdot mol^{-1}$.[16] This is because they use one-electron expansions and basis sets that are relatively small and rely on extensive parametrization to improve the results. Chemical accuracy can be reached, for example, with Weizmann-1 and Weizmann-2 (W1 and W2) methods[45] and several of their variants, along with some approaches belonging to the correlation-consistent composite approach (ccCA) hierarchy.[46] These typically employ the "golden standard" *N*-electron expansion in quantum chemistry, the coupled cluster method with singles, doubles, and perturbative triples (CCSD(T)) extrapolated to the complete basis set limit.[47] Such methods can typically be applied to molecular systems with up to 20 heavy non-hydrogen atoms. At the highest level are methods such as W3 and W4,[48,49] most variants of the highly accurate extrapolated *ab initio* thermochemistry (HEAT) protocol,[50] and the methodology of Feller, Peterson, and Dixon (FPD).[51,52] All three of these methods typically go beyond the CCSD(T) level and can achieve MADs that are even at sub-$kJ \cdot mol^{-1}$ level. However, owing to the high computational cost of the methods, their application range is limited to molecules with only a few heavy atoms.

In the following sections, the three composite methods most relevant to the current work, namely W1X-1, CBS-QB3, and FPD, are discussed in more detail to give an overview of the approximations made in deriving them and the overall level of their performance in calculating one of the fundamental thermochemical properties, the gas-phase enthalpy of formation of molecules.

4.2 W1X-1

Among the various composite methods, the W1 recipe was one of the first to reach chemical accuracy for medium-sized systems. The procedure was published by Jan Martin and Glênisson de Oliveira in 1999,[45] and its later variants all aim to reduce the computational cost of the original method and thereby broaden its application scope.[16]

The W1X-1 variant was published by Bun Chan and Leo Radom in 2012.[53] It starts with a density functional theory (DFT) level optimization at the B3LYP/cc-pV(T+*d*)Z level of theory, augmented by a vibrational analysis

applying a scale factor of 0.985 in the evaluation of the zero-point energy (ZPE) and enthalpy correction terms. The energy of the molecule in question is then calculated as a sum of four different terms: $E_{\text{HF-CABS}}$, $E_{\Delta\text{CCSD-F12b}}$, $E_{\Delta(\text{T})}$, and $E_{(\text{C+R})}$.

The first three terms, $E_{\text{HF-CABS}}$, $E_{\Delta\text{CCSD-F12b}}$, and $E_{\Delta(\text{T})}$, extrapolate the separate non-relativistic frozen core (FC) energy components HF-CABS, ΔCCSD-F12b, and Δ(T) to the complete basis set limit using cc-pVDZ-F12 and cc-pVTZ-F12 (HF-CABS and ΔCCSD-F12b), and aug′-cc-pV(D+*d*)Z and aug′-cc-pV(T+*d*)Z (Δ(T)) basis sets. The extrapolation formula

$$E_{\text{L}} = E_{\text{CBS}} + AL^{-\alpha}, \tag{XVIII}$$

where L is the cardinal number of the basis set (either 2 or 3) and α is a method-specific exponent (5, 3.6725, and 2.0436 for HF-CABS, ΔCCSD-F12b, and Δ(T), respectively), is used. The HF-CABS method calculates the Hartree-Fock (HF) energy augmented with a complementary auxiliary basis singles (CABS) correction that aims to reduce the incompleteness error in the HF energy resulting from the use of a finite basis set. The ΔCCSD-F12b component, as implied by its name, involves explicitly correlated CCSD-F12b level energy calculations that show much more rapid basis-set convergence than the common canonical CCSD variant. Last, the perturbative triples component Δ(T) is added at the canonical CCSD(T) level that uses smaller basis sets than those employed in the CCSD-F12b calculations due to the faster-converging but more computationally demanding Δ(T) energy.

The fourth term, $E_{(\text{C+R})}$, calculates the combined core correlation and scalar relativistic correction using 2nd order Møller–Plesset perturbation theory (MP2) and cc-pCVTZ basis set. The correction is obtained as the energy difference between two calculations performed on one hand using an all-electron relativistic Douglas-Kroll-Hess (DKH) Hamiltonian and on the other hand within the non-relativistic FC framework. Spin–orbit corrections are typically taken into account for atoms using experimental reference values.

There are two computational bottlenecks in the W1X-1 approach. The CCSD-F12b method uses vast amounts of scratch disk space for integral storage, whereas the CCSD(T) calculation represents the most time-consuming part. At the time of writing, the biggest molecules that could be treated at the W1X-1 level within a reasonable time frame are triphenylphosphine (PPh_3) and the corresponding oxide ($OPPh_3$). These systems have up 20 non-hydrogen atoms in a computational point group C_1; the actual point group of the molecules is a non-Abelian C_3 that is not typically implemented in most integral evaluation packages. Such calculations require up to three weeks of wall clock time per job using 8 CPU cores (Intel Xeon Gold 6140), 120 GB of memory per core, and 8 TB of fast SSD scratch disk space.

The W1X-1 method has been benchmarked against the standard gas-phase enthalpies included in the G2/97 and G3/99 test sets and reaches MADs of 2.4 and 3.5 $\text{kJ} \cdot \text{mol}^{-1}$, respectively.[53] However, it has become clear that some of the experimental reference values in the G2 and G3 data sets are highly suspicious or in some cases, such as with CF_2O,[54] clearly erroneous. Furthermore, the G2

and G3 data sets include molecules, such as O_3, for which either multiconfigurational approaches or coupled cluster ansatzes going beyond CCSD(T) should be used in the *N*-particle expansion.[55] If only a handful of these outliers are excluded from the statistical analyses, the MAD of W1X-1 with respect to the combined G2/97 and G3/99 test set drops below 3.0 $kJ \cdot mol^{-1}$; further reduction is expected if a more detailed analysis of the 200+ standard gas-phase experimental enthalpies of formation included in the test sets is conducted. Consequently, the root-mean-square deviation (RMSD) of W1X-1 is close to 3 $kJ \cdot mol^{-1}$ for typical chemical systems, giving 2σ and 3σ confidence intervals of ± 6 and ± 9 $kJ \cdot mol^{-1}$, respectively.

4.3 CBS-QB3

The first variants of the CBS group of composite methods were formulated by George Petersson and colleagues in the late 1980s.[56] The ansatz discussed herein, the CBS-QB3 method,[57] is a modification of the original CBS-Q recipe to use geometries and frequencies calculated with DFT.[58]

At the heart of the original CBS-Q method are five non-relativistic computational steps employing the FC framework.[58] First, the geometry of the molecule is optimized at the UHF/6-31G† level augmented with a frequency calculation employing a scale factor of 0.91844. The 6-31G† basis set is a modification of the 6-31G* set that combines *sp*-type functions from the 6-31G set with polarization exponents from the 6-311G** set. Next, a second optimization is carried out at the MP2/6-31G† level, and this structure is used for energy evaluations at UMP2/6-311+G(3*d*2*f*,2*df*,2*p*), MP4(SDQ)/6-31+G(*d*(*f*),*d*,*p*), and QCISD(T)/6-31+G† levels of theory. The basis set expressions used above indicate different polarization sets for third-, second-, and first- row atoms, respectively.

The baseline energy is provided by E_{UMP2}, which is augmented with a CBS extrapolation E_{CBS}. Next, $E_{\Delta MP4}$ and $E_{\Delta QCISD(T)}$ corrections are added by calculating the differences between MP4(SDQ)/6-31+G(*d*(*f*),*d*,*p*) and MP2/6-31+G(*d*(*f*),*d*,*p*), and QCISD(T)/6-31+G† and MP4(SDQ)/6-31+G† level energies, respectively. Further terms are then included to account for ZPE (E_{ZPE}), spin contamination (E_{spin}), and core correlation (E_C), though the last one is included only for sodium atoms. Finally, an empirical overlap interference correction term E_{emp} is added to arrive at the final CBS-QB energy. It should be noted that not only is E_{emp} based on experimental data (dissociation energies) but so also is E_{spin} (dissociation energies, ionization potentials, and electron affinities).

The CBS-QB3 model uses the general design philosophy of CBS-Q and replaces the geometry-optimization and frequency-calculation steps with B3LYP/6-311G(2*d*,*d*,*p*) geometries and frequencies (scale factor of 0.99) and also updates QCISD(T) method to CCSD(T).[57] As a final improvement, the authors recommended augmenting the computational results for atoms with atomic spin–orbit corrections from experimental references.

The CBS-QB3 method has been benchmarked against the standard gas-phase enthalpies included in the G2/97 test set and obtains MAD and RMSD values of 4.5 and 5.1 kJ · mol^{-1}, respectively.[57] However, as noted above, these are most likely slightly overestimated due to the inclusion of erroneous experimental values and some highly problematic systems in the reference set. Consequently, the 2σ and 3σ confidence intervals of CBS-QB3 can be estimated to be ± 9 and ± 13 kJ · mol^{-1}, respectively, for conventional molecular systems. If the statistical analysis also included molecules from the G3/99 test set, the confidence intervals would be slightly higher. Even though no such data are readily available, a recent benchmark study using standard gas-phase enthalpies of formation for medium-size organic molecules, as reported in the Active Thermochemical Tables as a reference set, gave 2σ and 3σ confidence intervals of ± 14 and ± 21 kJ · mol^{-1}, respectively, for CBS-QB3.[59] Taking all of the above into account, CBS-QB3 is significantly less accurate than W1X-1 but also considerably faster, as its bottleneck CCSD(T) calculation takes only some hours for molecules such as PPh_3 and $OPPh_3$ using the same hardware as described above.

4.4 FPD

The FPD approach has its origin in the work conducted in the 1990s by the authors David Feller, Kirk Peterson, and David Dixon.[60] Unlike most composite methods, the FPD approach does not refer to a single well-defined computational protocol or recipe, but rather describes a systematic, stepwise pathway to approach the exact energy of molecular systems.[51,52] Thus, FPD is far from being a black-box method and the user needs to make well-justified choices of how far the pathway is traveled in each case.

The two cornerstones of the FPD approach are the CCSD(T) method (within the FC approach) and correlation consistent basis sets up to the cardinal number 9, that is, aug-cc-pV9Z and aug-cc-pV(9+*d*)Z, extrapolated to the CBS limit.[51,52] The slowly converging valence correlation problem is separated from core correlation and scalar relativistic effects that are included as additional corrections at the CCSD(T) level using the DKH Hamiltonian with both approaches employing appropriate basis sets. A 1st order diagonal Born-Oppenheimer correction (DBOC) can be included at the FC-CCSD level using correlation consistent basis sets, typically up to the cardinal number 3. ZPE and enthalpy corrections are calculated at the same level of theory as the geometry optimization is performed, which, again, depends on the system in question and available computational resources (typically CCSD(T) with as high a cardinal number in the basis set as possible). The ZPE and enthalpy corrections use the harmonic approximation and are, therefore, augmented with anharmonicity corrections typically modeled at the FC-MP2 level. Higher-order corrections, that is, beyond CCSD(T), can be included within the framework of coupled cluster methods using CCSDT, CCSDTQ, or CCSDTQ5, as well as with explicit and estimated FCI, all approaches typically taken up to the level of cc-pV5Z basis set.

These calculations are often limited to the treatment of valence electrons, but they can also be conducted for core correlation, provided that the cardinal number of the basis set is adjusted accordingly. Last, computational results for atoms are augmented with atomic spin–orbit corrections from experimental references.

Considering the nature of the FPD approach, it is impossible to give a single MAD for its performance in calculating standard gas-phase enthalpies of formation of molecular species. However, in present-day application scenarios of the approach, it goes clearly beyond chemical accuracy and in many cases yields results that are more accurate than the best experimental calorimetric results with 2σ confidence intervals in the sub-kJ · mol^{-1} range.[16,51,52]

5 GROUP CONTRIBUTION METHODS

The previous Chapter discussed the calculation of thermochemical properties of molecules with composite quantum chemical methods. It ended with a notion that the most accurate methods available, such as the FPD approach, do not pale in comparison with the best experimental approaches. At this point, a touch of realism from Norm Cohen and Sidney Benson is perhaps needed:[61]

> "In the best of all possible worlds, a pharmaceutical chemist, cytologist, or paleobotanist interested in exploring the structure and reactivity of a hypothetical compound would simply turn on her 99th generation desktop supercomputer, input some minimum number of descriptive parameters, and apply Schrödinger's equation to calculate detailed (and accurate) potential energy surfaces, structural parameters, and energy relationships in the time it takes to rinse out a coffee cup. Alas, the inexorable progress of hardware, software, and brainware notwithstanding, we who would welcome that state of affairs face a vanishingly small probability of experiencing it in our professional lifetimes."

The quote is from the year 1993 and, much to the computational chemist's dismay, can be reiterated even today. Yes, computers and methods have evolved, but, no, the level at which a pharmaceutical chemist, cytologist, or paleobotanist could conduct the proposed calculations in the time it takes to do dishes has not yet been reached. Even though it is reassuring to know that composite methods can yield highly accurate results, the inability to apply these methods to all but the smallest of chemical systems creates frustration. Hence, the need for robust, fast, and accurate methods for the estimation, if not prediction, of thermodynamic properties of molecules still exists. As it happens, this is the realm of group contribution methods.

5.1 Basics of group contribution methods

Ever since the establishment of Dalton's atomic theory in the early 1800s, chemists and physicists have pondered whether molecular properties beyond mass would behave additively and could be estimated from the properties of their

atomic constituents. A particularly illustrative early example comes from Gervaise Le Bas, who collected decades of experimental work on molecular volumes to simple additivity principles in the early years of the 20th century.[62] Since that time, it has been understood that the additivity of molecular properties is not strictly fulfilled for anything except atomic and molecular masses. Nevertheless, the additivity principle generates a very useful approximate framework that allows the prediction of many molecular properties with great accuracy and speed.

Following Rafiqul Gani,[63,64] the fundamental working principle of many group contribution methods can be written in the form of a simple equation:

$$X = \sum_{i=1}^{m} a_i A_i + \sum_{j=1}^{n} b_j B_j + \sum_{k=1}^{o} a_k C_k + X_0, \qquad \text{(XIX)}$$

where X is the property to be estimated, A_i, B_j, and C_k are 1st, 2nd, and 3rd order group contributions of type i, j, and k, X_0 is a constant, and a_i, b_j, and c_k specify the number of times groups of type i, j, and k appear in the molecular representation of the compound. Equation XIX is linear as it is typically used so for the calculation of thermodynamic properties. However, it can also be made non-linear or modified in numerous other ways, all depending on the actual molecular property in question. Regardless of the actual details of Equation XIX, it is immediately evident that it is of far greater simplicity than the Schrödinger equation and can be solved even for very large molecular systems in the time it takes to wash a coffee mug. All that is required to solve it are the group contributions A_i, B_j, and C_k (tabulated values), the coefficients a_i, b_j, and c_k (fixed by the identity of molecule in question), and the constant X_0 (not necessarily even present).

The key building blocks of many group contribution methods are 1st order primary groups.[63,64] They can even be atoms or bonds, but typically they are atomic groups that can be used to create representations of molecular systems and are transferable between different molecular systems. For example, methanol CH_3OH and ethyl acetate $CH_3CH_2OC(O)CH_3$ can be represented using 1st order groups CH_3 (1) and OH (1), and CH_3 (2), CH_2 (1), and OC(O) (1), respectively, with the number of times the group appears in the molecular representation given in parentheses. It is immediately evident that there are innumerable ways to define the 1st order groups, meaning that different group contribution methods are, in general, mutually incompatible, even though they would focus on the description of the same molecular property. At the same time, it is equally easy to appreciate the working principle of group contribution methods as the five 1st order groups given above function analogously to LEGO® bricks and allow the description of even some very complex molecules with relatively few different types of building blocks.

In a typical scenario, the 1st order groups contain information on atoms and their nearest neighbors, that is, a group consists of a polyvalent central atom and the ligands bound to it.[63,64] For example, the 1st order groups present in ethyl acetate could be written as C-(C)$(H)_3$ (2), C-(C)$(H)_2$(O) (1), O-$(C)_2$ (1), and C-(C)(O)(O_d) (1), where the atoms in parentheses indicate the ligands, while the first atom, separated from the rest by a hyphen, denotes the central atom. The numeric

subscripts give the number of each type of atom connected to the central atom, while the subscript d is used to specify a C=O double bond so that the groups are unambiguous.

While 1st order groups suffice for surprisingly many purposes, they cannot appropriately handle, for example, all types of isomerism.[63,64] An illustrative example is *cis*- and *trans*-alkenes, such as *cis*- and *trans*-2-butene, which can be represented with the same set of 1st order groups. Thus, all predictions based on 1st order groups alone would give identical results for the two isomers, yet every chemist would immediately argue that the proximity of the two methyl groups in the *cis*-isomer cannot be neglected. A simple fix for the problem is to establish a correction term, in other words, a 2nd order group contribution or a non-nearest neighbor interaction (NNI), whose purpose is to capture long-range structural information that the 1st order groups are unable to transmit.

In many group contribution methods, the aforementioned two orders of groups suffice.[63–65] Because all aspects of bonding that the primary 1st order groups do not describe can be treated, at least in principle, with a correction term that is conceptually of higher order than the first one, there is really no need for 3rd order groups, nor is there an unambiguous way to divide different corrections into different orders. Nevertheless, the next level of approximation can be introduced, and 3rd order groups defined for molecules with, for example, fused aromatic rings or cage structures.[64] In other words, 3rd order groups are often used to describe long-range corrections than extend further than those in the 2nd order.

There is one caveat: in older literature on the topic, a method based on atomic contributions and atom additivity is defined as being a 0th order method, which means that methods based on bond contributions and bond additivity are 1st order, methods based on atomic groups and group additivity are 2nd order, and methods considering the ligands of the ligands of a central atom, that is, components and component additivity, are 3rd order.[65] Thus, all group contribution methods are, by this definition, 2nd order methods and can then have 1st, 2nd, and 3rd order groups. It is therefore important to keep in mind whether one is talking about a 2nd order method or a 2nd order group because these are not synonymous.

The success or failure of group contribution methods hinges on two factors: how well the additivity approximation holds and how accurate are the data used to obtain the individual group contributions through fitting. Experience gathered over the past 100+ years has shown that the additivity approximation is a very useful one as all chemistry students learn to estimate reaction enthalpies with the help of bond enthalpy data very early on at their studies. The Achilles heel of group contribution methods is therefore the underlying reference data, and an accurate and reliable data set is imperative to the success of the method. For many molecular properties, there exist ample amounts of good quality data that can be used to derive group contribution values. However, the same cannot be said of all thermodynamic properties and all molecular systems imaginable. Problems arise especially when group contribution methods are applied to

molecular systems outside the field of typical organic chemistry, that is, to molecules containing heteroatoms, such as organoboron, -silicon, and -phosphorus compounds, which are highly problematic systems for experimental calorimetry.[66]

As already mentioned, the field of group contribution method is vast and ever expanding. Thus, it is an impossible task to review all different methodologies described in the scientific literature over the past century. Consequently, a choice was made to briefly outline the basics of the most common method relevant to the current work, the Benson Group Increment Theory (BGIT), whereas other group contribution methods are largely omitted.

5.2 Benson Group Increment Theory (BGIT)

The foundations of the group contribution method of Sidney Benson and Jerry Buss, often known by the acronym BGIT, were established in 1958.[65] At first, the method was able to treat only hydrocarbons, which is a typical starting point for group contribution methods even in modern times due to the vast amount of experimental data available for these systems. However, Benson and co-authors greatly expanded the method, and only 10 years after its inception, a wealth of groups involving the elements C, H, O, N, and S and halogens were included in the published tables along with those containing the elements P, B, Sn, Pb, Cr, Zn, Ti, V, Cd, Al, Ge, and Hg.[66] Since then, BGIT has been expanded further, and a comprehensive account of the early decades of its development can be found in the second edition of Benson's book.[67]

One development of BGIT that deserves a special mention is its splitting into three mutually inconsistent group contribution approaches that slowly took place during the 1980s and 1990s. As a result, the original formulation of BGIT, included in Benson's book from 1976 in its "final" form,[67] is complemented with two slightly modified and extended versions. The first modification was created by Norm Cohen and Benson,[61,68] and, during the same time frame, another one was published by Eugene Domalski and Elisabeth Hearing.[69,70] The work of Cohen and Benson can be thought of as the successor to the original formulation of BGIT, but it does include a significant amount of updated data and contains revised values even for some of the most fundamental group contributions, such as the universal methyl group.[61,68] The work of Domalski and Hearing is much broader and widens the application area of BGIT into liquid and solid phases for elements C, H, O, N, and S and halogens.[69,70] Furthermore, Domalski and Hearing also developed several aspects of BGIT and introduced ideas such as long-range methyl repulsion terms for tertiary and quaternary carbon atoms, which replaced Benson's original formulations with conceptually simpler ones.

The methods by Cohen and Benson and Domalski and Hearing have not remained the only reincarnations of the original BGIT; more have been published over the years, such as the vast re-evaluation by John Holmes and Christiane Aubry.[71,72] This represents an unfortunate situation because the new methods

are typically highly specific and incompatible not only with each other but also with the original formulation of BGIT and those of Cohen and Benson and Domalski and Hearing.[73–75] Moreover, many of these new formulations of BGIT have not found such widespread use, for which reason they remain mostly scientific curiosities that nevertheless often extend BGIT to new application areas.

BGIT is a 2nd order method that uses 1st order (Benson) groups consisting of a polyvalent central atom and the ligands bound to it.[66,67] In many cases, the ligands are atoms, but, in some cases, such as with terminal groups –CO and –CN, they can also be atom groups or super atoms, as they are sometimes called. Specific notation is used to differentiate among bonding schemes. For example, C_d refers to a doubly bonded carbon, whereas C_B is used for an aromatic one. In addition to primary groups, BGIT includes various correction terms, 2nd order groups, to deal with effects such as isomerism, methyl repulsion, and ring strain.

In BGIT, group contribution values exist for standard enthalpy of formation, entropy, and heat capacity.[66,67] To calculate any of these, Equation XIX can be used. For enthalpy and heat capacity, $X_0 = 0$, but for entropy, this term is used to take into account symmetry-related entropy that is not simply additive. In such a case,

$$X_0 = -R \ln \sigma + R \ln \eta, \qquad \text{(XX)}$$

where σ is the molecule symmetry number and η is the number of possible optical isomers. Thus, the first term in Equation XX takes into account entropy from the total symmetry number of the molecule and the second one takes into account entropy due to optical isomerism.

As an elementary example of the practical use of BGIT, the standard gas-phase enthalpy of formation of ethanol CH_3CH_2OH can be calculated. The molecule consists of three Benson groups, C-(C)(H)$_3$, C-(C)(H)$_2$(O), and O-(C)(H), all present only once in the molecule. The corresponding group contribution values are −42.26, −32.90, and −159.33 kJ · mol^{-1}, respectively, giving a total of −234.49 kJ · mol^{-1}.[69,70] The reference value for ethanol is −234 ± 2 kJ · mol^{-1}, in excellent agreement with the estimate.

As discussed above, a group contribution method is only as good as the underlying parametrization. Likewise, it has already been mentioned that the lack of experimental thermodynamic data for many types of compounds is a serious obstacle in wider utilization of BGIT or any other group contribution method, for that matter. However, BGIT also has many internal limitations, of which two illustrative examples are given here.

In the traditional formulation of BGIT, ring systems pose problems for 2nd order correction terms.[66,67] Specifically, while it is straightforward to split a ring into 1st order primary groups, these groups are identical to those in linear molecules. While this might be a valid approximation for large rings, smaller ring systems are often strained, which needs to be factored in as a correction term. The traditional way of doing this has involved assigning a unique 2nd order group for each different ring correction. Because there are practically endless number of ways to form all-carbon and heteroatomic rings and then link, fuse, or cage

them with each other, such assignment is an enormous task. Clearly, a more systematic and automated method for dividing complex ring systems into concise sets of transferrable components is required and has, in fact, recently been proposed.[76]

A second example of an internal limitation in BGIT is its inability to treat weak intramolecular interactions such as hydrogen bonds. A simple example best illustrates the problem. The compound 3-hydroxypropenal is a simple hydrocarbon with both a carbonyl group and a hydroxyl group as well as a C=C double bond. It is an interesting small organic species that has recently been detected in the interstellar medium for the first time.[77] The molecule can have both *Z*- and *E*-isomers, of which the *Z*-form has an intramolecular hydrogen bond. If BGIT is applied to Z-3-hydroxypropenal, it predicts it to have the same thermodynamic properties as *E*-3-hydroxypropenal even though their standard enthalpies of formation must differ by a factor of a single O−H ⋯ O hydrogen bond, that is, approximately 20 $kJ \cdot mol^{-1}$. Such a problem can only be fixed by defining new 2nd order groups that introduce correction factors for hydrogen bonds as well as for other related intramolecular interactions. While such corrections have been reported in the literature, they are not universal and can only be used for highly specific types of compounds.[78]

6 RESULTS AND DISCUSSION

The purpose of this work was to use high-level quantum chemical composite methods to calculate standard gas-phase enthalpies of formation, entropies, and heat capacities for a wide variety of compounds of phosphorous, silicon, and boron. Further, the work was extended to use these data to derive new Benson group contributions for these elements, which could, in turn, be employed in estimating thermodynamic properties of compounds that have not been subjected to accurate experimental studies and/or cannot be treated with high-level theoretical methods. The foundations of this work were laid out by Benson and colleagues in one of their review papers in 1969:[66]

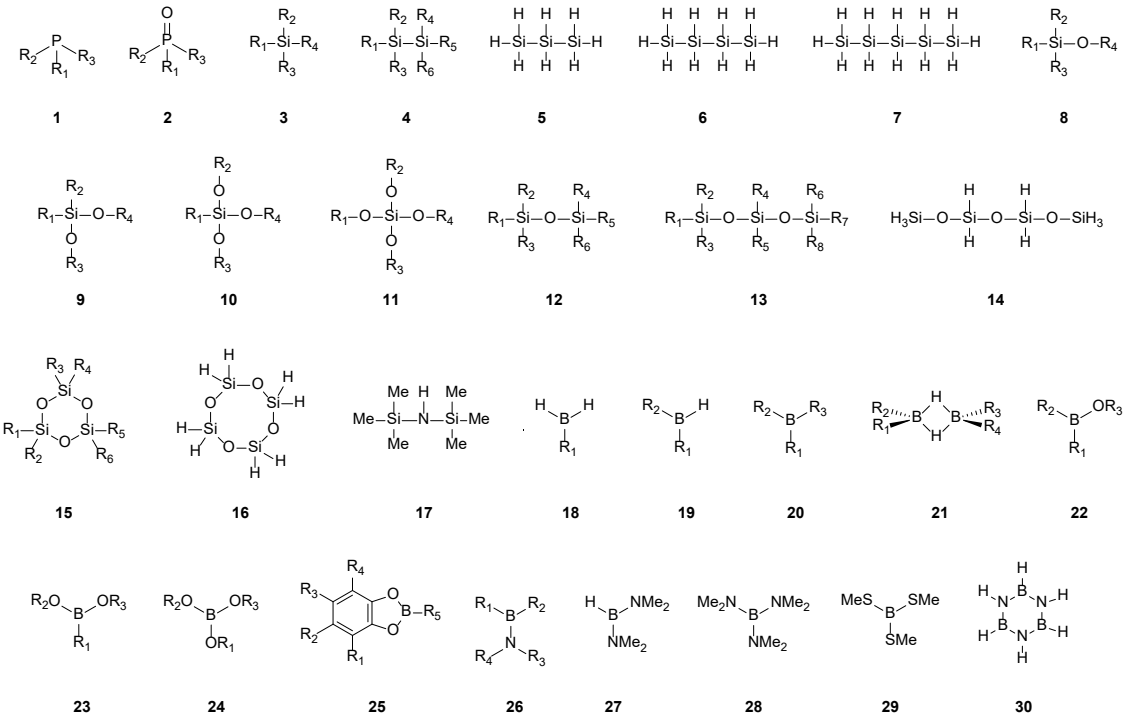
> "…the inconsistencies in the gaseous heat of formation of organosilicon compounds are made apparent by the failure to construct a reproducible set of group values."

It is now well established that the pre-1970 calorimetric data on silicon compounds were affected by incomplete combustion, and these values have, for the most part, been removed from thermodynamic libraries.[42,79] However, what remained in the databases was less than comprehensive and the above inconsistencies have not been resolved even in the 50 years following the publication of Benson's work. This stems from the fact that virtually no new experimental calorimetric, data on organosilicon compounds has surfaced within the past 30 years.[42]

The situation with boron is as grim as with silicon: reliable calorimetric work was highly problematic prior to the advent of fluorine-containing combustion promoters in the 1960s, and virtually no new or updated results have been published in decades.[80,81] Almost the same story can be told about many phosphorus compounds, in which case the problems in calorimetry were related to the formation of a mixture of acids instead of just orthophosphoric acid.[82,83] The separation and quantitative analysis of these products is by no means an overwhelming task, but it needs to be performed individually for each combustion reaction investigated. In many cases, the older published data have not been updated accordingly and might even be based on red phosphorus as the standard state.[83]

6.1 Thermodynamic properties

In this work, standard gas-phase enthalpies of formation, entropies, and heat capacities were calculated for 38 phosphines and phosphine oxides (**1** and **2**), 42 monosilanes (**3**), 7 polysilanes (**4**−**7**), 31 silanols and alkoxysilanes (**8**−**11**), 70 acylic siloxanes (**12**−**14**), 8 cyclic siloxanes (**15** and **16**), 1 silylamine (**17**), 40 monoboranes (**18**−**20**), 7 diboranes (**21**), 15 borinic acid derivatives (**22**), 23 boronic acid derivatives (**23**), 11 boric acid derivatives (**24**), 11 catecholboranes (**25**), 7 aminoboranes (**26**−**28**), one thioborate (**29**), and borazine (**30**). The results were reported in Papers **I**−**IV**. Both parent compounds as well as ones with alkyl (Me = methyl, Et = ethyl, Pr = propyl, ^{i}Pr = isopropyl, Bu = butyl, ^{s}Bu = *sec*-butyl, ^{t}Bu = *tert*-butyl, 3-Pe = 3-pentyl), alkenyl (Vi = vinyl, All = allyl), aryl (Ph = phenyl, *p*-Tol = para-tolyl) and/or halogen substituents were considered. All calculations were performed with the high-level W1X-1 thermochemical recipe[53], and the size of the examined systems was limited by the scaling of the method and the available hardware resources. For comparative purposed, all calculations were also performed with the CBS-QB3 method.[57]



Comparing the calculated standard gas phase enthalpies of formation to their experimental counterparts proved challenging. A critical review of the original literature reports revealed that many values often quoted as experimental are, in fact, based either partially of fully on theoretical estimates, such as the Franklin group equivalence method[84] or the computer-analyzed data compilation by Pedley and Rylance.[85] Furthermore, even though some data had clearly been obtained from experiments, the following derivations might include one or more

quantities that had been estimated rather than measured. This was often the case regarding the vast works of Skinner[86] or the thermochemical compilations of Becerra and Walsh.[79] For this reason, the calculated thermochemical data were also compared to results from other composite quantum chemical methods of even higher accuracy, such as W2[45] and FPD.[51,52]

At this point, it should be mentioned that during the course of this vast work, it was realized that the atomic reference values used in Papers **I** and **II** were inadvertently based on unrestricted MP2 energies even though the composite W1X-1 protocol uses restricted open-shell wave functions throughout.[53] This leads to atomic energies with sub-kJ · mol^{-1} errors, but the effect multiplies when standard gas-phase enthalpies of formation are determined from the data through calculation of total atomization energies. For this reason, an addition/correction was published as Paper **IV**, and it reports the corrected values for all data in the original Paper **II** with no changes in conclusions. Updated values of all data published in Paper **I** are reported herein, with Table 1 giving the W1X-1 standard gas-phase enthalpies of formation of phosphines and phosphine oxides based on the correct ROMP2 atomic energies. For comparison, the original UMP2 data are included in Table 1, as is also the case for the relevant experimental values.[87–91] It should be noted that the W1X1-ROMP2 values in Table 1 also include atomic spin-orbit correction terms to ensure that the calculated numbers are fully comparable to those given in Papers **III** and **IV**. For phosphines and phosphine oxides, the spin-orbit correction is mostly negligible, but it becomes less so for systems with multiple Si and F atoms or substituents with many carbon centers (phenyl).

The data in Table 1 as well as the results in the original papers allowed the identification of compounds for which the calculated and experimental standard gas-phase enthalpies of formation differ by more than 2–3σ. This is the case for, for example, triphenylphosphine oxide in Table 1 with a calculated enthalpy of formation that is significantly more endothermic than the experimental value.[90] When conducting these analyses, other computational data were used as additional reference points. As already noted, the thermodynamic properties of compounds **1–30** were also calculated with the CBS-QB3 method that functioned as sort of an internal standard. Furthermore, G3X data by Dorofeeva et al. were used in Paper **I**,[92–94] results from very high-level W2 calculations in Papers **II** and **IV**, and reference enthalpies based on the FPD approach in Paper **III**.[95–97] Such extensive analyses allowed us to conclude that many of the fundamental standard gas-phase enthalpies of formation in silicon and boron chemistry are most likely significantly in error and should be revised accordingly. For example, there are two experimental values for the standard gas-phase enthalpy of formation of triphenylborane: 130.1 ± 8.4 kJ · mol^{-1} based on its enthalpy of hydrolysis[98] and 155.4 ± 8.4 kJ · mol^{-1} based on its sublimation enthalpy.[99] The two values are statistically different even within 3σ confidence interval, and they are both significantly more endothermic than our best W1X-1 prediction, 293.3 kJ · mol^{-1}, with an expected 3σ confidence interval of ± 9 kJ · mol^{-1}.

Table 1. Gas-phase standard enthalpies of formation ($\Delta H_f°$ 298K, kJ · mol^{-1}) calculated for phosphines and phosphine oxides discussed in Paper **I** at W1X-1 level using corrected atomic reference values (ROMP2) and adding spin-orbit correction terms. For convenience, the values published in Paper **I** (UMP2) and experimental data (Exptl.) are also included.[87–91]

Molecule[a]	$\Delta H_f°$ 298K W1X-1 (UMP2)	$\Delta H_f°$ 298K W1X-1 (ROMP2)	$\Delta H_f°$ 298K Exptl.	Molecule[a]	$\Delta H_f°$ 298K W1X-1 (UMP2)	$\Delta H_f°$ 298K W1X-1 (ROMP2)	$\Delta H_f°$ 298K Exptl.
PH_3	9.7	10.2	5.4 ± 1.7	OPH_3	–204.6	–202.6	
PH_2Me	–17.7	–16.3	–14.1 ± 8.0	OPH_2Me	–277.0	–274.1	
$PHMe_2$	–55.5	–53.3		$OPHMe_2$	–348.1	–344.4	
PMe_3	–102.7	–99.7	–97.0 ± 4.6	$OPMe_3$	–417.5	–413.0	–431.7 ± 8.0
PH_2Et	–37.4	–35.3	–36.5 ± 1.5	OPH_2Et	–294.1	–290.4	
$PHEt_2$	–89.5	–85.7	–89.6 ± 2.1	$OPHEt_2$	–383.3	–378.0	
PEt_3	–151.9	–146.4	–152.7 ± 2.8	$OPEt_3$	–466.4	–459.4	
PMe_2Et	–119.5	–115.6		$OPMe_2Et$	–434.0	–428.6	
PH_2Pr	–60.6	–57.6		OPH_2Pr	–316.9	–312.4	
$PH_2{}^iPr$	–62.1	–59.1		$OPH_2{}^iPr$	–321.2	–316.7	
$PH_2{}^sBu$	–82.3	–78.4		$OPH_2{}^sBu$	–341.4	–336.1	
$PH_2{}^tBu$	–93.6	–89.8		$OPH_2{}^tBu$	–354.0	–348.7	
PH_2Ph	123.0	128.5		OPH_2Ph	–130.5	–123.6	
$PHPh_2$	222.6	233.0		$OPHPh_2$	–57.7	–45.8	
PPh_3	-	327.4	320.2 ± 4.7	$OPPh_3$	-	30.8	2.8 ± 7.0
PHMePh	84.3	90.6		OPHMePh	–203.3	–195.5	
PMe_2Ph	39.4	46.5		$OPMe_2Ph$	–274.2	–265.6	
$PMePh_2$	177.4	188.6		$OPMePh_2$	–128.4	–115.6	
PMeEtPh	19.5	27.4		OPMeEtPh	–293.7	–284.2	

[a] Used abbreviations: Me = methyl, Et = ethyl, Pr = propyl, ^{i}Pr = isopropyl, ^{s}Bu = *sec*-butyl, ^{t}Bu = *tert*-butyl, and Ph = phenyl.

6.2 Benson group contribution values

The calculated W1X-1 thermodynamic properties of phosphorus, silicon, and boron compounds **1–30** were used to derive Benson group contributions for 24, 60, and 52 phosphorus-, silicon-, and boron-based Benson groups and group pairs in the published papers. The Domalski–Hearing version of Benson Group Increment Theory was used throughout.[69,70] The determined group contributions are published in Paper **III** and **IV** for boron- and silicon-based groups, respectively. Because the values given in Paper **I** for phosphorus-based groups are based on incorrect atomic reference energies and do not include atomic spin-orbit correction terms, the revised values of standard gas phase enthalpies of formation are published here in Table 2.

As the Benson group contribution values have no physical meaning, a comparison of the group contributions determined in this work to anything available in the literature must be made with caution. However, some general observations can be made. First, Dorofeeva and colleagues have created an exhaustive database of group contribution values for phosphorus-based groups,

some of which overlap with those given in Table 2.[92–94] However, their work is based on Cohen's formulation of Benson's approach, whereas the current work follows that of Domalski and Hearing. Consequently, a value published in one data set cannot be easily transferred to another without exhaustive determination of correct conversion factors. Second, when preparing the work for publication, two papers by Janbazi and co-workers were published that focused on Benson group contribution values for silicon-based groups.[100,101] The work of Janbazi and co-workers is also based on Cohen's revised formulation and, upon closer analysis, establishes a group contribution method of its own, because different values were used for groups C−(C)(H)$_3$ and C−(H)$_3$(Si). Such a choice represents a significant step away from all Benson-type group additivity approaches that uniformly fix the contribution from a methyl group (except for its physical state) no matter what atom it is attached to. This is a very convenient choice that is typically made to avoid linear dependencies, that is, having too many unknowns and too few equations. It is therefore not surprising that the group contribution values reported by Janbazi and co-workers differ greatly from the numbers given by us in Paper **IV**. Third, as explained in detail in the published papers, the reported group contribution values form self-consistent sets that reproduce the underlying W1X-1 level data with good or very good accuracy, as they obviously should if the additivity approximation holds. The same cannot be said of Benson's original group contributions for boron[66] or those derived by Becerra and Walsh for silicon.[79] In both cases, the group contribution values have significant error estimates, which easily lead to highly inaccurate predictions of thermochemical properties with little to no practical value.

Table 2. Thermochemical Benson group and group pair contributions for standard enthalpies of formation ($\Delta H_f°$ 298K, kJ · mol^{-1}) of phosphorus-based groups discussed in Paper **I** at W1X-1 level using corrected atomic reference values (ROMP2) and adding spin-orbit correction terms.

Benson Group	$\Delta H_f°$ 298K	Benson Group Pair	$\Delta H_f°$ 298K
C-(H)$_2$(C)(P)	–16	P-(H)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(P)	59
C-(H)(C)$_2$(P)	6	P-(H)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(P)	95
C-(C)$_3$(P)	27	P-(C$_B$)$_3$ + 3 C$_B$-(C$_B$)$_2$(P)	120
P-(H)$_2$(C)	24	P-(C)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(P)	61
P-(H)(C)$_2$	31	P-(C)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(P)	93
P-(C)$_3$	28	P-(H)(C)(C$_B$) + C$_B$-(C$_B$)$_2$(P)	64
C-(H)$_2$(C)(PO)	–17	PO-(H)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	–193
C-(H)(C)$_2$(PO)	4	PO-(H)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(PO)	–184
C-(C)$_3$(PO)	24	PO-(C$_B$)$_3$ + 3 C$_B$-(C$_B$)$_2$(PO)	–176
PO-(H)$_2$(C)	–232	PO-(C)$_2$(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	–251
PO-(H)(C)$_2$	–261	PO-(C)(C$_B$)$_2$ + 2 C$_B$-(C$_B$)$_2$(PO)	–212
PO-(C)$_3$	–285	PO-(H)(C)(C$_B$) + C$_B$-(C$_B$)$_2$(PO)	–222

6.3 Application examples

The established group contribution values can be used to estimate the thermodynamic properties of large organophosphorus, -silicon, and -boron compounds that cannot be treated with high-level composite quantum chemical methods. The approach is not only fast but also accurate, and it was put into action in Papers **II** and **IV** by estimating the standard gas-phase enthalpies of formation of organosilicon species examined by Voronkov and colleagues using calorimetry.[102–107] The validity of these very comprehensive experimental accounts has been repeatedly questioned by Becerra and Walsh, who have suggested that the data are affected by systematic error.[42,79] This conclusion was based on the incompatibility of the results reported by Voronkov and colleagues with other well-established reference values and general trends.

A comparison between data reported by Voronkov and colleagues and results from the W1X-1 calculations performed in this work revealed exactly the type of inconsistencies described by Becerra and Walsh. However, only a handful of compounds out of several hundred studied by Voronkov and colleagues. could be subjected to such high-level analyses. Consequently, a comparison between experimental data and enthalpies of formation evaluated using Benson group contribution values was carried out in Paper **IV**, which allowed the analysis to be performed for roughly 40 alkylsilanes, alkoxysilanes, and cyclosiloxanes. The results clearly indicated that the experimental values of alkylsilanes must contain an unknown source of systematic error, as suggested by Becerra and Walsh, because they are consistently 40 $kJ \cdot mol^{-1}$ more exothermic than enthalpies obtained using Benson group contributions. In contrast, the data for alkoxysilanes and phenyl substituted cyclosiloxanes showed no similar systematic bias, and enthalpies estimated for trimethoxy- and triethoxysilanes with thioether substituents were found to be in excellent agreement with experimental values. With such a varying performance, it is recommended that the experimental results reported by Voronkov colleagues be flagged in thermodynamic databases and treated with caution until validated or refuted on case-by-case basis.

In a similar fashion, the usefulness of Benson group contribution values was demonstrated in Paper **III** by using them to assess the quality of reference standard enthalpies of formation for a series of organoboron compounds.[86,108,109] The reference values cannot be considered fully experimental because estimated quantities have been used to derive them. For this reason, some of them have been assigned with uncertainties as high as ± 30 $kJ \cdot mol^{-1}$. The results clearly supported this practice as the values with the highest uncertainties were found to be the furthest away from estimates based on Benson group contributions. In these cases, an additional check on the data was performed by carrying out an explicit W1X-1 calculation. In contrast, good agreement between reference values and those given by Benson group contributions was noted in cases where

experimental uncertainties were more reasonable, thereby building confidence that the estimations made in deriving the reference values are entirely justified.

7 CONCLUSIONS AND OUTLOOK

The goal of this work involved three interrelated objectives: first, to use high-level quantum chemical composite methods to calculate accurate thermodynamic properties for over 300 compounds of phosphorus, silicon, and boron with little or no experimental data available; second, to compare the theory-based results with their experimental counterparts and data from prior computational studies to reveal inconsistencies, outliers, or even systematic errors; and third, to use the computational results to derive group additivity contributions for almost 150 phosphorus-, silicon-, and boron-based groups within the framework of the Domalski-Hearing version of Benson Group Increment Theory.

As shown by the results of this study, the composite quantum chemical method chosen for the task, namely W1X-1, clearly proved its worth in yielding very accurate results within a reasonable time frame. Molecules containing up to 20 non-hydrogen atoms could be investigated and such systems are among the biggest ever treated at this level of theory. The calculated thermodynamic properties form an extensive benchmark data set to which further work and results can be compared. Furthermore, considering the much smaller uncertainties associated with the W1X-1 results in comparison to the bulk of existing experimental data, it is highly recommended that the standard gas-phase enthalpies of formation reported in this work are employed in all thermochemical analyses and calculations targeting high accuracy.

The computational limits set by the W1X-1 theory allowed the treatment of a sufficient number of prototype compounds that are needed to derive the most important Benson group contributions for each element investigated. Consequently, this work led to both revised and new group contribution values for phosphorus-, silicon- and boron-based groups, which allowed the straightforward extension of the Benson Group Increment Theory to many new compound classes of the three aforementioned elements. Moreover, the new sets of Benson group contributions described herein enable the thermodynamic properties of new and unknown chemical species to be estimated quickly, accurately, and inexpensively. This is a highly valuable asset, for example, in any industrial environment, where heat balance calculations, automated reaction

mechanism generators, and detailed process planning are used regularly. Standard enthalpy of formation is also one of the most important thermochemical properties in the performance prediction of explosives.

Group contribution methods might seem archaic and, therefore, of little use in the era of high-performance computing and petaFLOPS-level supercomputers. However, as demonstrated by the results of this work as well as those of many others, these methods certainly have their place in the toolbox of chemists and are extremely useful for many purposes. It is certainly true that they will eventually be replaced by more accurate protocols, but such a day is not yet in the foreseeable future. Recent developments in reduced-cost, linear-scaling, and local CCSD(T) approaches are continuously pushing forward the application range of the "gold standard" of quantum chemistry, but they will not change the fact that these methods deliver results within days rather than within minutes as required by many applications where thermodynamic properties of molecules are used. As it will still take years, possibly even decades, before quantum computing becomes truly mainstream, the best avenue forward in developing group contribution methods is their marriage with machine-learning algorithms, a change that is already taking place. However, machine learning can only be as good as the data it is fed. For this reason, the continued importance of reliable thermodynamic data, be they experimental or computational, cannot be over-emphasized.

SUMMARY IN FINNISH

Yksi viimeisten vuosien keskeisistä puheenaiheista on ollut energia: sen hinta, tuotanto ja kulutus sekä sen käytön seuraukset. Keskustelun aiheena ovat olleet niin eri energialähteiden saatavuus, kustannukset, turvallisuus ja ympäristövaikutukset kuin energian tuotantoon, varastointiin ja kuljetukseen liittyvät näkökulmat. Kaiken tämän keskiössä on kemia, sillä kaikkiin energiamuotoihin liittyy niiden tuotannossa, siirrossa ja varastoinnissa käytettävät ja syntyvät kemialliset yhdisteet sekä kemiallisiin reaktioihin liittyvät energianmuutokset. Ensiarvoisen tärkeää on tietää se, tarvitseeko jokin reaktio energiaa vai vapauttaako se sitä, ja kuinka paljon. Toisin sanoen, on tunnettava prosessissa mukana olevien kemiallisten yhdisteiden termodynaamiset ominaisuudet. Tätä tietoa tarvitaan energiantuotannon ohella esimerkiksi myös kemian teollisuuslaitosten prosessien suunnittelussa ja niiden optimoinnissa.

Kemiallisista yhdisteistä tietoa keskitetysti kokoavan Chemical Abstracts Service (CAS) -palvelun tietokannassa on tällä hetkellä yli 200 miljoonaa kemiallista yhdistettä, joista termodynaamiset ominaisuudet tunnetaan tarkasti vain muutamalle tuhannelle. Suunnatonta aukkoa tietämyksessä voidaan täyttää kahdella eri tavalla. Yhdisteiden termodynaamisia ominaisuuksia voidaan määrittää laboratoriossa tehtävien kokeellisten mittausten avulla tai niitä voidaan laskea kvanttikemiallisilla menetelmillä tietokoneavusteisesti.

Kokeellisen termodynamiikan mittausmenetelmistä tärkein on kalorimetria, joka soveltuu erinomaisesti pääasiassa hiiltä ja vetyä sisältäville orgaanisille molekyyleille, mutta muuttuu huomattavasti vaativammaksi niin laitteistojen kuin teknisen osaamisen ja kokemuksen suhteen, kun kyse on heteroatomeja, kuten fosforia, piitä ja booria, sisältävistä yhdisteistä. Termokemian mittauksiin erikoistuneita kemian tutkimuslaboratorioita on nykyään harvassa ja yhdisteiden termodynaamisten ominaisuuksien suuresta kysynnästä huolimatta vuosittain julkaistaan hyvin rajallisesti uusia tuloksia. Julkaistusta datasta osa sisältää myös aiemmin mitattujen arvojen uudelleenmäärityksiä, joissa tyypillisesti pienennetään aikaisempien tulosten epätarkkuutta tai korjataan havaittuja virheitä.

Vaihtoehdoksi kokeellisten termodynamiikan menetelmien rinnalle ja osin myös niiden tilalle on tullut kvanttikemiallinen laskenta ja erityisesti niin kutsutut yhdistelmämenetelmät eli termokemialliset reseptit. Näillä menetelmillä päästään jopa kokeellisia menetelmiä parempaan tarkkuuteen, mutta saavutetulla tarkkuudella on hintansa. Jo muutamia kymmeniä raskaampia atomeja sisältävien molekyylien kohdalla tulosten saamiseen voi mennä viikkoja tai kuukausia tehokkaiden työasemien laskenta-aikaa yhtä yhdistettä kohden. Kvanttikemiallisten menetelmien soveltamisessa on myös useita rajoituksia, sillä esimerkiksi menetelmien vaatimia kantajoukkoja ei ole määritetty suinkaan kaikille jaksollisen järjestelmän alkuaineille.

Jos kemiallisten yhdisteiden termodynaamisia ominaisuuksia tarvitaan nopeasti tai suurelle joukolle yhdisteitä, ovat sekä kokeelliset mittausmenetelmät että kvanttikemiallinen laskenta kumpikin liian hitaita käytettäväksi. Tällaisissa

tapauksissa on mahdollista hyödyntää niin kutsuttuja ryhmäkontribuutio-menetelmiä, joissa molekyylien ominaisuuksia pyritään arvioimaan niiden sisältämien kemiallisten ryhmien määrän ja tyypin perusteella. Menetelmän taustalla olevan approksimaation mukaan kukin ryhmä antaa samansuuruisen kontribuution molekyylin ominaisuuteen riippumatta siitä, mikä molekyyli on kysymyksessä. Näin termodynaamisia ominaisuuksia voidaan arvioida nopeasti suurillekin molekyyleille yksinkertaisten yhteen- ja kertolaskujen avulla. Menetelmän ongelmana luonnollisesti on, että kunkin ryhmän vaikutus laskettavan suuren arvoon pitää olla määritetty ennakkoon, mutta olemassa olevat taulukot ryhmäkontribuutioista eivät ole kovinkaan kattavia tai taulukoitujen ryhmäkontribuutioiden arvot perustuvat kokeelliseen dataan, jonka tarkkuus on huono. Ehkä tunnetuin ryhmäkontribuutiomenetelmistä, joka on myös niistä laajimmin käytetty ja parametrisoitu laajimmalle joukolle kemiallisia yhdisteitä, on Sidney Bensonin kehittämä Benson Group Increment Theory eli tuttavallisemmin BGIT.

Tässä väitöskirjatutkimuksessa laskettiin tarkkojen kvanttikemiallisten menetelmien avulla muodostumisentalpia, entropia ja ominaislämpökapasiteetti yli kolmellesadalle orgaaniselle fosforia, piitä ja booria sisältävälle yhdisteelle kaasufaasissa ja standarditilassa. Suurinta osaa kyseisistä yhdisteistä tutkittiin tällä tarkkuudella ensimmäistä kertaa. Saatuja tuloksia verrattiin kokeelliseen dataan sekä aiempien laskennallisten tutkimusten tuloksiin. Tällä tavalla voitin osoittaa kokeellisesta datasta löytyvän runsaasti epäjohdonmukaisuuksia sekä myös karkeita ja systemaattisia virheitä. Monissa tapauksissa tutkimuksen tuottamat arvot yhdisteiden termodynaamisille ominaisuuksille ovat kokeellisia arvoja huomattavasti tarkempia, mikä puoltaa työssä määritettyjen arvojen käyttämistä jatkosovelluksissa.

Laskettuja termodynaamisia ominaisuuksia hyödynnettiin lisäksi määritettäessä uudet ja päivitetyt Bensonin ryhmäkontribuutiot lähes 150:lle fosforia, piitä ja booria sisältävälle ryhmälle käyttäen Domalskin ja Hearingin versiota BGIT-menetelmästä. Määritettyjen ryhmäkontribuutioiden avulla on mahdollista arvioida niin olemassa olevien kuin vielä tuntemattomien kemiallisten yhdisteiden termodynaamisia ominaisuuksia nopeasti, hyvällä tarkkuudella ja riippumatta yhdisteiden koosta. Vastaavanlaista lähestymistapaa on käytetty aikaisemmin fosforin ja piin ryhmäkontribuutioiden määrittämiseksi, mutta raportoiduista tutkimuksista yksikään ei pohjaudu Domalskin ja Hearingin laajennukseen Bensonin menetelmästä, vaan käyttää pohjana sen kanssa yhteensopimatonta Cohenin ja Bensonin menetelmää. Boorin yhdisteiden tapauksessa tehty työ on tiettävästi ainoa laatuaan ja päivittää Bensonin aikanaan julkaisemat ryhmäkontribuutiot huomattavasti tarkempiin tuloksiin.

Kokonaisuutena voidaan todeta, että työ tuotti runsaasti uutta numeerista tietoa kemiallisten yhdisteiden termodynaamisista ominaisuuksista sekä laajensi merkittävästi kyseisten ominaisuuksien arvioinnissa käytetyn Bensonin ryhmäkontribuutiomenetelmän käyttöaluetta. Työn tuloksilla on runsaasti sovelluskohteita. Niitä voidaan hyödyntää esimerkiksi teollisuuden prosessisuunnittelussa tai tieteellisessä tutkimuksessa. Mikä tärkeintä, niiden

avulla voidaan määrittää termokemiallisia ominaisuuksia yhdisteille, joita ei vielä ole olemassa tai joiden käsittely laboratoriossa on vaarallista tai muutoin ongelmallista. Saatuja tuloksia voidaan hyödyntää myös kehitettäessä uusia ja parempia menetelmiä molekyylien termodynaamisten ominaisuuksien arviointiin esimerkiksi yhdistämällä keskenään ryhmäkontribuutiomenetelmät ja koneoppiminen.

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ORIGINAL PAPERS

I

BENSON GROUP ADDITIVITY VALUES OF PHOSPHINES AND PHOSPHINE OXIDES: FAST AND ACCURATE COMPUTATIONAL THERMOCHEMISTRY OF ORGANOPHOSPHORUS SPECIES

by

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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]

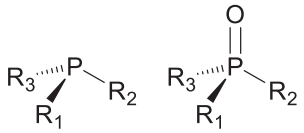
One of the most significant advantages of Benson group additivity method is its speed: thermochemical properties can be accurately estimated within a fraction of a second, irrespective of the size of the system in question. This can be contrasted with high-level composite quantum chemical methods that 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]



a **b**

	R_1	R_2	R_3
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	^{i}Pr	H	H
11	^{s}Bu	H	H
12	^{t}Bu	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 σ_{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_2Me)	−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_2Et)	−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_2Et)	−119.5	−116.7			365.9	124.1	175.6	255.2
9a (PH_2Pr)	−60.6	−61.2	−57.4		327.6	93.8	138.4	206.6
10a ($PH_2{}^iPr$)	−62.1	−63.3	−59.9		322.9	95.6	140.9	208.1
11a ($PH_2{}^iBu$)	−82.3	−81.6			356.3	117.9	174.4	258.6
12a ($PH_2{}^tBu$)	−93.6	−94.4	−93.0		347.8	121.5	179.7	262.2
13a (PH_2Ph)	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_2Ph)	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_2Me)	−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_2Et)	−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 ($OPMe_2Et$)	−434.0	−433.8			383.1	135.6	193.0	279.8
9b (OPH_2Pr)	−316.9	−320.8			344.9	102.0	155.5	231.8
10b ($OPH_2{}^iPr$)	−321.2	−325.7			345.3	106.3	155.6	228.6
11b ($OPH_2{}^iBu$)	−341.4	−344.1			376.1	126.7	189.2	282.0
12b ($OPH_2{}^tBu$)	−354.0	−358.2			368.7	132.6	195.3	282.9
13b (OPH_2Ph)	−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 ($OPMe_2Ph$)	−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.

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Keywords: Benson group additivity method, computational thermochemistry, composite methods, phosphines, phosphine oxides

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II

HIGH-LEVEL AB INITIO PREDICTIONS OF THERMOCHEMICAL PROPERTIES OF ORGANOSILICON SPECIES: CRITICAL EVALUATION OF EXPERIMENTAL DATA AND A RELIABLE BENCHMARK DATABASE FOR EXTENDING GROUP ADDITIVITY APPROACHES

by

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High-Level Ab Initio Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches

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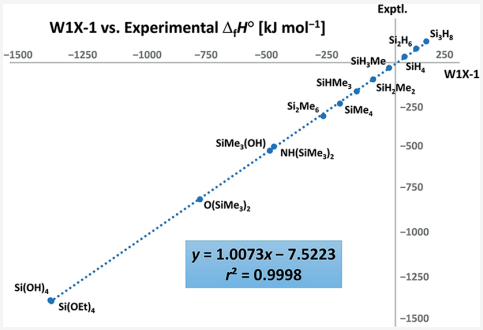
ABSTRACT: A high-level composite quantum chemical method, W1X-1, is used herein to calculate the gas-phase standard enthalpy of formation, entropy, and heat capacity of 159 organosilicon compounds. The results set a new benchmark in the field that allows, for the first time, an in-depth assessment of existing experimental data on standard enthalpies of formation, enabling the identification of important trends and possible outliers. The calculated thermochemical data are used to determine Benson group additivity contributions for 60 Benson groups and group pairs involving silicon. These values allow fast and accurate estimation of thermochemical parameters of organosilicon compounds of varying complexity, and the data acquired are used to assess the reliability of experimental work of Voronkov et al. that has been repeatedly criticized by Becerra and Walsh. Recent results from other computational investigations in the field are also carefully discussed through the prism of reported advancements.



INTRODUCTION

A central concept in thermochemistry is the standard enthalpy of formation of a compound, $\Delta_f H°$, the enthalpy change during the formation of one mole of a particular substance from its elements with all constituents in their standard states.[1] Standard enthalpies of formation are typically determined from experimentally measured standard enthalpies of combustion and by applying Hess's law of constant heat summation. This also elucidates the centrality of $\Delta_f H°$ in thermochemistry as the enthalpy change of any reaction, $\Delta_r H°$, can be calculated (eq 1) by taking the difference in the sum of standard enthalpies of formation of the products (i) and that of the reactants (j), with each value multiplied by its stoichiometric coefficient ν_n:

$$\Delta_r H° = \Sigma\nu_i \Delta_f H_i° - \Sigma\nu_j \Delta_f H_j° \quad (1)$$

Standard enthalpies of formation are often determined using calorimetry.[2] The approach is straightforward for many organic compounds and requires a measurement of the enthalpy of combustion of the compound in question along with literature data for the combustion products, such as CO_2, H_2O, and NO_x. Although simple in principle, combustion calorimetry is much more laborious in practice. For example, the required measurements of weight and temperature must be conducted to high precision and all undesirable side reactions, such as incomplete combustion or oxidation of the crucible, appropriately accounted for. Furthermore, reactions involving very small heat changes are challenging for combustion calorimetry, as is also true for compounds that are volatile, highly reactive, or slowly burning.

During the past two decades, high-accuracy quantum chemical methods have gained ground as important alternatives to accurately determine standard enthalpies of formation.[3] The Weizmann-1 (W1) method was the first widely applicable protocol to reach chemical accuracy (a mean absolute deviation, MAD, less than 4 kJ mol^{-1}) for second- and third-row compounds,[4] while more advanced methods, such as W4,[5] FPD,[6] and HEAT-QP,[7] are nowadays able to predict standard enthalpies of formation even at sub-kJ mol^{-1} precision. The caveat with using the most accurate methods is that they can only be applied to molecules with less than 10 non-hydrogen atoms, and even W1 and its variants can only effectively handle systems up to 20 heavy atoms.[3]

A practical alternative for obtaining thermodynamic data on larger molecules without conducting experimental measure-

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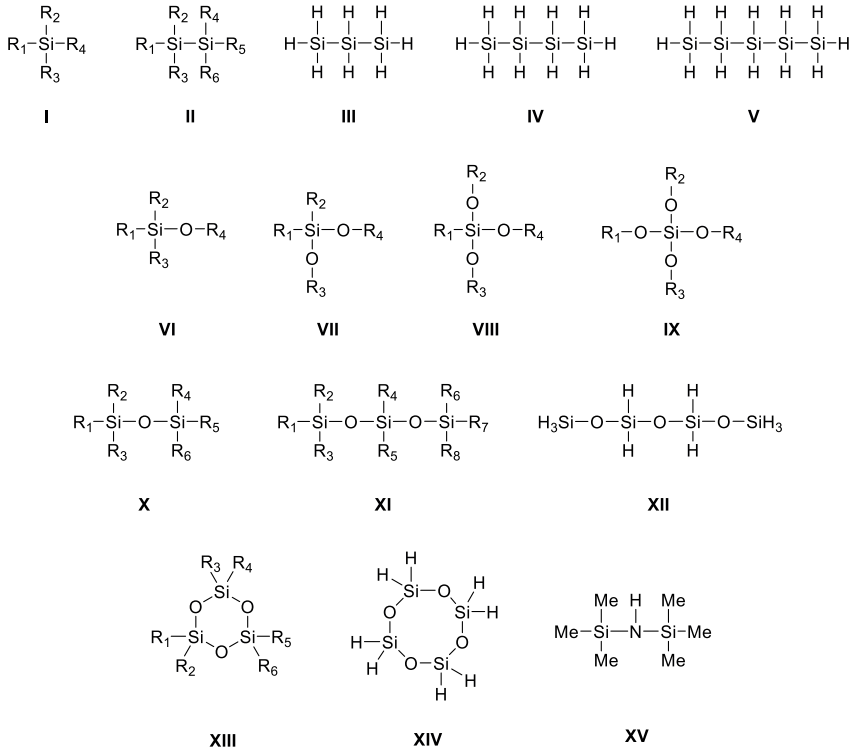
Chart 1. General Structures of Organosilicon Compounds 1−159 Considered in This Work and Their Division to Groups I−XV (R_1−R_8 = Alkyl, Alkenyl, Aryl, and/or Fluorine Substituents, See Table 1)



ments is to use group additivity approaches. These are based on the century-old empirical notion that the properties of molecules can be accurately estimated by dividing them into groups whose contributions to physical properties remain nearly constant from one system to another.[8] The scheme originally proposed by Benson and Buss,[9] later extended to liquid and solid phases by Domalski and Hearing,[10,11] has become one of the most successful realizations of this kind. While it might seem archaic in the era of high-performance computing, the approach is very powerful when data are needed on a large group of molecules, so that quantum chemical methods, be they of any kind, would be too time-consuming. This is especially true in combustion chemistry and automated reaction mechanism generation in particular.[12]

The accuracy of group additivity approaches naturally depends on two factors: how well the additivity approximation holds and how accurate the data used to determine the group contributions are. Even though the additivity of properties is not strictly fulfilled beyond atomic and molecular masses, experience accumulated over the past 50+ years has shown that Benson's methodology is able to achieve chemical accuracy for many organic systems, that is, molecules composed of atoms H, B, C, N, O, F, P, S, Cl, Br, and I.[13,14] Thus, important keys to the success of group additivity approaches are the treatment of molecules that are problematic for additivity, such as strained or sterically congested systems, and ensuring that the reference thermochemical data used to determine the group contributions are of the highest quality.

As noted by Benson,[15] multiple inconsistencies in the experimental standard enthalpies of formation of organosilicon compounds prevented the determination of an internally consistent set of additivity contributions for silicon-based groups. It is now well established that many of the pre-1970 calorimetric experiments on silicon compounds were in error due to incomplete combustion,[16] and the associated values have largely been removed from thermochemical compilations. Unfortunately, what remained in the data libraries became less than comprehensive and the situation has not improved significantly over the years. As repeatedly discussed by Walsh and Becerra in their excellent reviews on the thermochemistry of organosilicon compounds,[17−19] the science of calorimetry has become almost extinct, and only a very few experimental values have been published for silicon-based species during the past 25 years. Furthermore, even the ones that have been published, such as the very comprehensive works of Voronkov et al.,[20−25] have been questioned to be affected by systematic error(s) due to their incompatibility with other literature values that are often associated with high uncertainties themselves.

The aim of the current contribution is threefold. First, we use the high-level W1X-1 composite method[26] to calculate the standard enthalpies of formation of 159 organosilicon species. To the best of our knowledge, this is the first comprehensive effort to establish a high-accuracy ab initio thermochemical benchmark database for organosilicon compounds. The calculated values are compared with experimental data, where available, allowing us to assess their accuracy and to pinpoint outliers and other inconsistencies. Of special interest are the results published by Voronkov et al.,[20−25] in which case our aim is to determine whether the practice of flagging their data in thermochemical reviews is entirely justified. Second, we compare our results to the earlier CCSD(T)/CBS benchmark

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values of Feller and Dixon,[27] as well as to the recent computational works of Burcat and Goos[28] and Janbazi et al.[29,30] The data reported by Janbazi et al. are found to be partially inconsistent with the other results, which is not only problematic by itself but also because the G4 enthalpies have been used as reference data in establishing group additivity contributions. Third, after carefully evaluating the reliability of our thermochemical data, we use the W1X-1 results to derive group additivity contributions for the standard gas-phase enthalpy of formation, $\Delta_f H^\circ_{298K}$, entropy, S°_{298K}, and heat capacity, C_p, for 60 Benson groups and group pairs involving silicon. We show that the group contributions form internally consistent sets and compare them to those reported by Walsh and Becerra[18] and Janbazi et al.[29,30] We also use our group contributions to determine the standard enthalpies of formation for several organosilicon species examined by Voronkov et al.[20−25] that could not be calculated directly with the W1X-1 method simply due to molecular size. This allows a thorough assessment of the experimental data published by Voronkov et al. for possible systematic errors.

■ COMPUTATIONAL DETAILS

Following our previous work,[31] the composite method W1X-1[26] was used for the calculation of standard gas-phase enthalpies of formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), entropies (S°_{298K}, J K^{-1} mol^{-1}), and heat capacities (C_p, J K^{-1} mol^{-1}) for 159 organosilicon compounds (Chart 1), which include 42 monosilanes (**1−42**, group **I**), 7 polysilanes (**43−49**, groups **II−V**), 31 silanols and alkoxysilanes (**50−80**, groups **VI−IX**), 70 acyclic siloxanes (**81−150**, groups **X−XII**), 8 cyclic siloxanes (**151−158**, groups **XIII** and **XIV**), and 1 silylamine (**159**, group **XV**) with alkyl (Me = methyl, Et = ethyl, ^{i}Pr = isopropyl, ^{s}Bu = *sec*-butyl, and 3-Pe = 3-pentyl), alkenyl (Vi = vinyl), aryl (Ph = phenyl), and/or fluorine substituents. The size of the investigated systems was limited by the computational cost of the W1X-1 method that became prohibitive for molecules with more than ca. 35 atoms, requiring up to 10 TB of fast disk space for integral storage and weeks of wall-clock time even when the codes were executed in parallel. To this end, we chose to use the CBS-QB3 method[32] for comparison purposes as it performed equally well with W1X-1 in our previous study on phosphines and phosphine oxides with only a fraction of the computational cost of W1X-1.

All structures were optimized with the Gaussian 16[33] program package at the B3LYP[34−37] level of theory using 6-311G(2d,d,p)[38,39] (CBS-QB3) or cc-pV(T+d)Z[40,41] (W1X-1) basis sets. For systems with multiple low-lying conformers, such as compounds with more than one ethyl or ethoxy substituent, extensive conformational scans were performed with the B3LYP/cc-pV(T+d)Z method to locate the global minimum on the potential energy surface. Total energies were computed for the lowest energy conformer of each molecule using the W1X-1[26] and CBS-QB3[32] protocols.

The CBS-QB3 method was used as implemented in the Gaussian 16 package.[33] W1X-1 energies were obtained by the protocol of Chan and Radom using the Molpro code.[26,42−44] Specifically, HF-CABS,[45] CCSD-F12b,[46,47] and CCSD(T)[48,49] methods with cc-pVDZ-F12, cc-pVTZ-F12,[50−53] aug′-cc-pV(D+d)Z, and aug′-cc-pV(T+d)Z[40,41] basis sets were used to extrapolate three nonrelativistic energy components, $E_{\text{HF-CABS}}$(cc-pVT/DZ-F12), $E_{\Delta\text{CCSD-F12b}}$(cc-pVT/DZ-F12), and $E_{\Delta(\text{T})}$(aug′-cc-pV(T/D+d)Z), to the complete basis set (CBS) limit using the extrapolation formula $E_L = E_{CBS} + AL^{-\alpha}$,[54] where L is the cardinal number of basis sets (2 or 3), and α is an adjustable parameter (5, 3.6725, and 2.0436 for HF-CABS, ΔCCSD, and Δ(T), respectively).[26] The cc-pCVTZ basis set was used with FC-MP2 and DKH-MP2[55,56] methods to obtain a combined core and scalar relativistic correlation term $E_{\Delta(\text{C+R})}$ as a difference of the two single-point energies.[57,58]

For selected compounds, very high-level W2 energies were calculated with the Molpro code using the established procedure.[4,59] The W2 method follows a similar protocol as W1X-1 with basis set extrapolation up to the pentuple-ζ level and without employing the F12 ansatz. Furthermore, CCSD(T)/MTsmall calculations, not MP2/cc-pCVTZ, are used to obtain the combined core and scalar relativistic correlation term.[4,48,49] Because of the size of the systems in question, coupled cluster level geometry optimizations in W2 were replaced with density functional level calculations, as originally recommended by Martin and de Oliveira,[4] using the B3LYP/cc-pV(T+d)Z combination augmented with Grimme's empirical dispersion correction (GD3) with Becke−Johnson damping.[60,61]

For the determination of standard enthalpies of formation, heat capacities, and entropies, the density functional level harmonic vibrational frequencies were scaled with 0.985 (W1X-1 and W2) or 0.990 (CBS-QB3). The calculation of entropies and heat capacities was carried out within the rigid rotor-harmonic oscillator approximation and treating rotation modes involving single bonds as hindered rotors using the procedure implemented in Gaussian 16.[62] A periodicity of 3 and a symmetry number of 3 were used for functional groups with local C_3 symmetry, while 3 and 1 were used for other functional groups.

Standard gas-phase enthalpies of formation $\Delta_f H^\circ_{298K}$ were obtained using the atomization energy approach. For multi-conformational molecules, the experimental enthalpy of formation reflects a Boltzmann distribution of conformers having statistically significant populations at 298 K. In contrast, our calculations use the most stable conformer for each molecule. This choice was made because Bolzmann averaging has been shown to lead to a correction that is similar in magnitude but opposite in sign to the correction for low-frequency internal rotations.[63] Hence, both corrections should be treated on equal footing, that is, either included or omitted. Considering the number of compounds investigated in this study and the level of theory employed, the calculation of these correction terms would have been a prohibitively expensive task.

Reference values for the enthalpies of formation of gaseous atoms and thermal corrections for elements in their standard states were taken directly from the NIST/JANAF tables for elements H, C, N, O, and F.[64] However, the commonly employed NIST/JANAF value for the standard enthalpy of formation of gaseous Si carries a very large uncertainty of 8.0 kJ mol^{-1}, as opposed to elements H, C, O, and F, whose uncertainties are an order of magnitude smaller. For this reason, the theoretical W4 enthalpy of formation of gaseous Si, 452.71 kJ mol^{-1}, reported by Karton and Martin was used as it has a statistical uncertainty of only 0.8 kJ mol^{-1}.[65] The atomization energies were also corrected for atomic spin−orbit (SO) coupling effects, a practice not uniformly followed in the field. While this correction can be obtained through theory, we chose to employ the experimental values tabulated by Moore.[66]

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Table 1. Calculated Gas-Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), Entropies (S°_{298K}, J K^{-1} mol^{-1}), and Heat Capacities (C_p, J K^{-1} mol^{-1}) of Monosilanes 1−42, Polysilanes 43−49, Silanols and Alkoxysilanes 50−80, Acyclic Siloxanes 81−150, Cyclic Siloxanes 151−158, and Silylamine 159[a]

			$\Delta_f H^\circ$ 298 K		S° 298 K	C_p 298 K	C_p 500 K	C_p 1000 K
group	molecule	chemical formula	W1X-1	CBS-QB3	W1X-1	W1X-1	W1X-1	W1X-1
I	1	SiH_4	35.9	27.0	225.2	34.7	51.0	76.2
	2	SiH_3Me	−23.8	−27.6	257.5	57.6	84.5	125.1
	3	SiH_3Et	−32.8	−34.4	302.1	79.5	117.5	175.5
	4	SiH_3Vi	96.9	94.3	288.5	68.5	100.6	146.6
	5	SiH_3Ph	124.8	130.6	330.3	103.5	171.8	258.7
	6	$SiH_3{}^iPr$	−52.7	−52.7	331.9	104.3	154.2	227.9
	7	$SiH_3{}^sBu$	−72.3	−70.2	366.2	126.2	186.8	278.0
	8	SiH_3(3-Pe)	−90.6	−86.8	402.4	144.8	218.5	328.1
	9	SiH_2Me_2	−85.9	−85.1	301.4	82.6	118.9	174.2
	10	SiH_2EtMe	−94.8	−91.9	342.9	104.1	151.4	224.5
	11	SiH_2MeVi	34.0	35.9	329.3	93.4	134.9	195.6
	12	SiH_2MePh	63.3	70.5	389.9	133.0	210.5	312.0
	13	$SiH_2Me{}^iPr$	−114.9	−110.7	372.0	129.0	188.1	276.7
	14	$SiH_2Me{}^sBu$	−134.2	−128.0	406.5	150.7	220.4	326.7
	15	SiH_2Me(3-Pe)	−151.7	−143.8	439.5	171.5	255.2	378.7
	16	SiH_2Et_2	−103.7	−98.8	373.0	125.8	183.9	274.7
	17	SiH_2EtPh	52.7	62.9	426.8	154.2	242.6	362.1
	18	SiH_2Vi_2	153.5	156.6	344.5	105.1	151.6	217.3
	19	SiH_2Ph_2	210.3	223.4	462.3	184.9	302.5	449.8
	20	$SiHMe_3$	−149.9	−145.2	337.6	109.3	153.9	223.5
	21	$SiHEtMe_2$	−158.7	−152.1	382.2	130.2	186.0	273.6
	22	$SiHMe_2Vi$	−30.6	−24.8	369.1	120.0	169.8	244.8
	23	$SiHMe_2Ph$	−2.2	8.5	429.8	159.6	245.4	361.2
	24	$SiHMe_2{}^iPr$	−178.7	−171.0	411.0	155.1	222.6	325.9
	25	$SiHMe_2{}^sBu$	−197.9	−188.4	444.8	177.1	255.3	375.9
	26	$SiHMe_2$(3-Pe)	−215.3	−204.3	477.9	197.8	289.8	427.7
	27	$SiHEtMePh$	−12.7	−0.8	461.4	182.6	279.0	411.9
	28	$SiHMeVi_2$	88.2	95.1	388.9	131.6	186.3	266.3
	29	$SiHMePhVi$	115.7	127.2	448.5	170.9	261.6	382.6
	30	$SiHVi_3$	207.8	215.4	411.8	141.2	201.4	287.4
	31	$SiHPhVi_2$	234.9	247.5	468.4	184.0	278.7	404.3
	32	$SiMe_4$	−215.0	−207.4	363.6	137.5	189.9	273.0
	33	$SiEtMe_3$	−223.7	−214.4	420.2	157.8	221.5	323.0
	34	$SiMe_3Vi$	−96.5	−87.6	406.5	147.7	205.2	294.1
	35	$SiMe_3Ph$	−68.4	−55.2	463.4	189.0	281.9	410.8
	36	$SiMe_2Vi_2$	21.9	31.8	421.9	158.4	221.0	315.4
	37	$SiEtMe_2Ph$	−78.8	−64.9	506.2	211.8	314.7	461.1
	38	$SiMe_2PhVi$	49.1	63.2	485.6	199.5	297.6	432.0
	39	$SiMe_2Ph_2$	76.0	94.0	535.2	242.4	375.0	549.0
	40	$SiMeVi_3$	139.9	150.1	438.8	170.3	237.8	337.0
	41	$SiMePhVi_2$	166.1	180.4	503.7	212.1	314.5	453.7
	42	$SiEt_4$	−251.9	−238.8	509.3	224.9	321.2	474.4
II	43	Si_2H_6	81.1	74.2	275.6	70.3	97.8	135.7
	44	Si_2H_5Me	22.9	20.1	331.6	94.5	131.5	184.6
	45	$Si_2H_4Me_2$	−34.6	−33.4	367.0	118.5	165.2	233.5
	46	Si_2Me_6	−280.3	−267.3	513.5	227.2	305.9	430.5
III	47	Si_3H_8	120.4	113.7	350.3	105.8	144.0	194.9
IV	48	Si_4H_{10}	158.4	151.7	415.4	141.9	190.4	254.2
V	49	Si_5H_{12}	196.1	189.4	481.1	177.7	236.7	313.4
VI	50	SiH_3OH	−280.1	−286.7	256.8	46.1	66.8	93.0
	51	SiH_2MeOH	−350.7	−352.4	297.6	70.7	101.0	142.1
	52	SiH_2EtOH	−359.3	−359.3	332.2	93.3	134.4	192.7
	53	$SiHMe_2OH$	−419.7	−417.7	337.4	97.5	136.2	191.4
	54	$SiMe_3OH$	−488.2	−483.4	375.9	125.0	171.6	240.7
	55	SiH_3OMe	−245.8	−253.7	300.2	63.1	93.4	141.3
	56	$SiH_2Me(OMe)$	−316.4	−319.7	340.7	87.8	127.5	190.4
	57	$SiHMe_2(OMe)$	−385.0	−384.9	380.3	115.0	162.9	239.7

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Table 1. continued

group	molecule	chemical formula	$\Delta_f H°$ 298 K		$S°$ 298 K	C_p 298 K	C_p 500 K	C_p 1000 K
			W1X-1	CBS-QB3	W1X-1	W1X-1	W1X-1	W1X-1
VII	58	$SiH_2(OH)_2$	−628.7	−633.2	280.0	62.9	85.1	110.3
	59	$SiH_2(OMe)_2$	−557.7	−565.7	365.7	92.1	136.0	206.2
	60	$SiHMe(OMe)_2$	−630.3	−635.1	404.2	115.0	169.4	255.0
	61	$SiHVi(OMe)_2$	−509.5	−513.6	430.8	128.7	186.5	276.6
	62	$SiHPh(OMe)_2$	−483.3	−482.7	487.2	171.2	263.3	393.3
	63	$SiMe_2(OMe)_2$	−702.3	−705.1	443.3	147.1	207.0	305.0
	64	$SiMeVi(OMe)_2$	−582.4	−584.6	469.1	156.0	221.7	325.9
	65	$SiMePh(OMe)_2$	−556.8	−555.0	524.0	200.6	301.9	446.5
	66	$SiVi_2(OMe)_2$	−462.6	−464.3	480.4	174.8	246.6	355.8
	67	$SiPhVi(OMe)_2$	−437.4	−435.4	543.3	225.6	335.8	487.8
	68	$SiPh_2(OMe)_2$	−412.4	−406.9	597.6	250.5	390.7	580.4
VIII	69	$SiH(OH)_3$	−985.9	−988.7	316.2	79.1	103.3	127.7
	70	$SiMe(OMe)_2OH$	−986.6	−992.3	440.7	137.1	190.0	273.0
	71	$SiEt(OMe)_2OH$	−994.3	−999.1	476.2	156.6	220.2	322.2
	72	$SiMe(OMe)_3$	−948.6	−957.0	480.5	162.0	227.1	333.1
	73	$SiEt(OMe)_3$	−956.7	−964.3	515.4	173.0	247.6	371.0
IX	74	$Si(OH)_4$	−1341.7	−1344.2	335.9	98.2	122.7	145.5
	75	$Si(OMe)_3OH$	−1232.3	−1243.4	466.8	143.3	199.3	289.1
	76	$Si(OEt)(OMe)_2OH$	−1267.5	−1277.0	501.6	174.1	243.2	349.4
	77	$Si(OEt)_2(OMe)OH$	−1302.8	−1310.8	533.2	199.1	280.2	401.7
	78	$Si(OMe)_4$	−1195.8	−1209.9	503.1	162.9	227.2	337.7
	79	$Si(OEt)\ (OMe)_3$	−1231.3	−1243.8	541.8	184.5	262.1	389.4
	80	$Si(OEt)_4$	−1337.7	−1345.7	636.2	252.8	369.2	545.4
X	81	$O(SiH_3)_2$	−339.7	−356.3	316.2	71.3	106.4	152.3
	82	$O(SiMe_3)(SiH_3)$	−550.7	−556.8	436.3	151.4	211.9	300.3
	83	$O(SiF_3)(SiH_3)$	−1605.9	−1620.9	383.3	99.0	131.6	166.2
	84	$O(SiH_2Me)(SiH_3)$	−410.7	−422.3	355.9	96.1	140.8	201.5
	85	$O(SiH_2Vi)(SiH_3)$	−289.3	−300.1	376.2	106.7	156.7	222.8
	86	$O(SiH_2Ph)(SiH_3)$	−259.6	−265.8	435.5	146.5	232.3	339.2
	87	$O(SiH_2F)(SiH_3)$	−759.8	−774.9	338.8	78.7	114.1	156.6
	88	$O(SiHMe_2)(SiH_3)$	−481.0	−489.3	403.8	123.6	176.4	251.0
	89	$O(SiHVi_2)(SiH_3)$	−241.3	−248.0	438.2	145.3	208.6	293.7
	90	$O(SiHF_2)(SiH_3)$	−1190.3	−1204.1	358.2	88.3	122.7	161.2
	91	$O(SiHMePh)(SiH_3)$	−332.7	−335.7	485.4	174.0	267.9	388.6
	92	$O(SiH_2Me)_2$	−481.4	−488.3	394.0	121.7	175.6	250.8
	93	$O(SiHMe_2)(SiH_2Me)$	−550.7	−555.1	439.7	149.1	211.1	300.3
	94	$O(SiH_2Ph)(SiH_2Me)$	−329.9	−330.6	476.2	171.7	266.9	388.4
	95	$O(SiMe_3)(SiH_2Me)$	−621.2	−622.5	478.1	176.9	246.7	349.6
	96	$O(SiHMe_2)_2$	−621.6	−621.7	486.5	176.5	246.7	349.7
	97	$O(SiMe_3)(SiHMe_2)$	−690.8	−689.1	533.2	204.3	282.2	399.0
	98	$O(SiMe_3)_2$	−760.0	−756.2	559.0	232.9	318.3	448.5
	99	$O(SiH_2Vi)_2$	−238.9	−244.5	440.4	142.6	207.2	293.4
	100	$O(SiH_2F)_2$	−1179.1	−1192.1	343.0	86.1	121.7	160.9
	101	$O(SiHF_2)(SiH_2F)$	−1607.7	−1619.7	380.9	96.0	130.4	165.6
	102	$O(SiF_3)(SiH_2F)$	−2022.4	−2035.4	394.9	106.4	139.3	170.6
	103	$O(SiHF_2)_2$	−2034.6	−2045.5	393.4	105.5	139.0	170.4
	104	$O(SiF_3)(SiHF_2)$	−2448.8	−2460.7	413.2	116.0	147.8	175.4
	105	$O(SiF_3)_2$	−2861.4	−2874.1	461.3	130.7	160.9	184.5
XI	106	$SiH_2(OSiH_3)_2$	−746.1	−771.7	412.6	110.5	163.2	228.7
	107	$SiH_2(OSiH_2Me)(OSiH_3)$	−816.3	−838.0	459.5	135.9	197.9	278.0
	108	$SiH_2(OSiH_2Vi)(OSiH_3)$	−695.9	−716.0	476.5	147.0	214.1	299.4
	109	$SiH_2(OSiH_2Ph)(OSiH_3)$	−665.7	−680.3	559.8	202.8	305.9	432.2
	110	$SiH_2(OSiH_2F)(OSiH_3)$	−1166.0	−1190.8	428.9	118.0	170.9	233.0
	111	$SiH_2(OSiMe_3)(OSiH_3)$	−958.5	−973.7	532.7	191.0	268.9	376.8
	112	$SiH_2(OSiHMe_2)(OSiH_3)$	−888.5	−905.8	489.9	163.0	233.2	327.4
	113	$SiH_2(OSiHF_2)(OSiH_3)$	−1596.1	−1620.1	446.1	127.7	179.6	237.7
	114	$SiH_2(OSiF_3)(OSiH_3)$	−2011.9	−2036.7	464.9	138.4	188.5	242.7
	115	$SiH_2(OSiH_2Me)_2$	−888.2	−904.2	500.4	161.6	232.7	327.3
	116	$SiH_2(OSiHMe_2)(OSiH_2Me)$	−959.5	−972.0	549.7	188.8	268.1	376.7

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Table 1. continued

group	molecule	chemical formula	$\Delta_f H°$ 298 K		$S°$ 298 K	C_p 298 K	C_p 500 K	C_p 1000 K
			W1X-1	CBS-QB3	W1X-1	W1X-1	W1X-1	W1X-1
	117	$SiH_2(OSiMe_3)(OSiH_2Me)$	−1029.4	−1039.9	568.5	216.6	303.7	426.1
	118	$SiH_2(OSiH_2F)_2$	−1585.0	−1607.1	445.5	125.8	178.6	237.3
	119	$SiH_2(OSiHMe_2)_2$	−1030.3	−1039.4	567.5	216.0	303.5	426.1
	120	$SiH_2(OSiMe_3)(OSiHMe_2)$	−1100.2	−1107.2	627.0	244.0	339.2	475.5
	121	$SiH_2(OSiMe_3)_2$	−1169.9	−1175.1	648.2	272.3	375.1	524.9
	122	$SiHMe(OSiH_3)_2$	−821.1	−843.2	460.5	137.5	198.5	278.1
	123	$SiHVi(OSiH_3)_2$	−699.2	−720.8	468.0	147.1	213.7	299.2
	124	$SiHPh(OSiH_3)_2$	−671.9	−689.0	530.4	188.5	290.3	415.9
	125	$SiHF(OSiH_3)_2$	−1178.3	−1203.6	433.8	120.3	171.9	233.3
	126	$SiHMe(OSiH_2Me)(OSiH_3)$	−892.1	−909.5	498.1	162.8	233.1	327.4
	127	$SiHMe(OSiHMe_2)(OSiH_3)$	−963.4	−977.0	526.2	190.3	268.7	376.9
	128	$SiHMe(OSiMe_3)(OSiH_3)$	−1033.0	−1045.1	572.5	218.3	304.3	426.2
	129	$SiHMe(OSiH_2Me)_2$	−962.9	−975.5	531.7	188.5	268.0	376.7
	130	$SiHMe(OSiHMe_2)(OSiH_2Me)$	−1034.4	−1043.4	566.6	215.9	303.5	426.2
	131	$SiHMe(OSiMe_3)(OSiH_2Me)$	−1104.1	−1111.3	604.3	243.9	339.1	475.5
	132	$SiHMe(OSiHMe_2)_2$	−1104.4	−1110.6	619.7	243.9	339.2	475.6
	133	$SiHMe(OSiMe_3)(OSiHMe_2)$	−1174.7	−1179.1	644.2	272.7	377.5	528.8
	134	$SiHMe(OSiMe_3)_2$	−1243.8	−1246.5	702.0	304.1	417.0	582.2
	135	$SiHF(OSiH_2F)(OSiH_3)$	−1594.8	−1622.9	454.0	136.3	188.1	246.0
	136	$SiHF(OSiHF_2)(OSiH_3)$	−2027.1	−2051.1	464.9	137.6	188.3	242.3
	137	$SiMe_2(OSiH_3)_2$	−894.7	−915.5	492.1	165.7	234.3	327.6
	138	$SiMe_2(OSiH_2Me)(OSiH_3)$	−965.5	−981.5	529.3	191.1	269.0	376.9
	139	$SiMe_2(OSiHMe_2)(OSiH_3)$	−1036.6	−1049.1	571.8	222.8	308.8	430.5
	140	$SiMe_2(OSiMe_3)(OSiH_3)$	−1106.2	−1116.9	620.1	251.6	345.0	480.1
	141	$SiMe_2(OSiH_2Me)_2$	−1036.0	−1047.4	562.1	216.8	303.8	426.2
	142	$SiMe_2(OSiHMe_2)(OSiH_2Me)$	−1107.2	−1115.0	625.4	245.0	339.7	475.8
	143	$SiMe_2(OSiMe_3)(OSiH_2Me)$	−1176.7	−1182.8	641.8	273.3	375.7	525.2
	144	$SiMe_2(OSiMe_3)_2$	−1316.6	−1317.9	718.3	329.0	447.2	624.1
	145	$SiMe_2(OSiHMe_2)_2$	−1177.1	−1182.3	656.1	272.0	375.2	525.2
	146	$SiMe_2(OSiMe_3)(OSiHMe_2)$	−1246.9	−1250.4	683.3	300.9	411.3	574.7
	147	$SiF_2(OSiH_3)_2$	−1598.9	−1625.4	436.9	131.1	181.0	238.2
	148	$SiF_2(OSiH_2F)(OSiH_3)$	−2017.1	−2043.8	461.6	138.7	188.7	242.6
	149	$SiF_2(OSiH_2F)_2$	−2434.9	−2460.5	477.5	146.2	196.4	247.0
XII	**150**	$O(SiH_2OSiH_3)_2$	−1151.9	−1186.1	494.3	150.0	220.1	305.1
XIII	**151**	$(OSiH_2)_3$	−1196.3	−1215.7	349.9	116.9	170.9	229.6
	152	$(OSiHMe)(OSiH_2)_2$	−1273.4	−1290.0	404.3	143.9	206.1	279.0
	153	$(OSiMe_2)(OSiH_2)_2$	−1348.1	−1362.9	437.4	171.9	241.8	328.4
	154	$(OSiHMe)_2(OSiH_2)$	−1350.2	−1363.8	438.1	171.0	241.4	328.4
	155	$(OSiMe_2)(OSiHMe)(OSiH_2)$	−1424.6	−1436.6	482.2	199.0	277.1	377.9
	156	$(OSiHMe)_3$	−1426.6	−1437.3	482.8	198.2	276.8	377.9
	157	$(OSiMe_2)_3$	−1648.3	−1653.8	583.4	282.5	384.0	526.2
XIV	**158**	$(OSiH_2)_4$	−1623.5	−1656.2	467.6	165.7	235.7	314.0
XV	**159**	$NH(SiMe_3)_2$	−472.0	−454.0	551.0	247.8	334.3	466.3

[a]Used abbreviations: Me = methyl, Et = ethyl, ^{i}Pr = isopropyl, ^{s}Bu = *sec*-butyl, 3-Pe = 3-pentyl, Vi = vinyl, and Ph = phenyl.

The computed W1X-1 thermochemical parameters were used to derive Benson group contributions for 60 silicon-based Benson groups and group pairs. The Benson group contributions were derived using a Convex Over and Under ENvelopes for Nonlinear Estimation (COUENNE) algorithm of the COIN-OR foundation[67] implemented in OpenSolver[68,69] and minimizing the squared differences between the computed thermochemical parameters and parameters calculated as sums of group contributions. Literature values were used for all carbon-based Benson groups, and entropy contributions were corrected for optical isomerism ($R \ln n$, where n is the total number of stereoisomers) as well as internal (σ_{int}) and external (σ_{ext}) symmetries ($-R \ln \sigma_{tot}$, where $\sigma_{tot} = \sigma_{ext}\Pi^i(\sigma_{int})_i$).[15] When deriving group contribution values, the methyl repulsion correction term of Domalski and Hearing was used for tertiary carbon atoms,[10,11] while ring strain was taken into account by using a single ring strain parameter for each ring size.[15] Instead of using a single unsubstituted (parent) compound to determine the strain parameter for a given ring, it was optimized for all compounds of a particular ring type during the fitting procedure.

To obtain unique and well-converged sets of group contributions from the fits, the values of some groups must be fixed to avoid linear dependencies. In the case of element−carbon bonds, this has typically been achieved by setting the values of the group E−(C)(H)$_3$ to be independent of element E and fixed to the value of C−(C)(H)$_3$, as initially chosen by Benson.[9] In the current case, this choice is not alone sufficient

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and the values of the group Si−$(C)_3(O)$ were set to match those of Si−$(C)_4$, following the practice of Becerra and Walsh.[18] Furthermore, the values of the group C_D−(C_D)(H)-(Si) also needed to be fixed and were adjusted to be the same as those determined for C_D−(C)(C_D)(H). The fits obtained using this procedure reproduced the original W1X-1 thermochemical data excellently in the case of enthalpies (MAD 0.8 kJ mol^{-1}, maximum deviation −6.5 kJ mol^{-1}) and heat capacities (MAD 1.0 J K^{-1} mol^{-1}, maximum deviation −10.6 J K^{-1} mol^{-1}), while slightly poorer performance was seen in the case of entropies (MAD 3.9 J K^{-1} mol^{-1}, maximum deviation 26.6 J K^{-1} mol^{-1}).

■ RESULTS AND DISCUSSION

Comparison of Calculated Gas-Phase Standard Enthalpies of Formation with Experimental Data. Before discussing the computational results (Table 1) in comparison with experimental data (Table 2), an analysis contrasting the W1X-1 values with those obtained with the CBS-QB3 method is warranted. Excluding data for the parent silane SiH_4 and a few of its monoalkyl derivatives, the CBS-QB3 enthalpies for monosilanes **I** are always slightly greater than those obtained with the W1X-1 method, leading to a positive mean signed deviation (MSD) between the two data sets of 7 kJ mol^{-1}. However, the opposite is true for all other groups. While the MSD values remain close to 0 for polysilanes **II**−**V** and silanols and alkoxysilanes **VI**−**IX**, −2 and −4 kJ mol^{-1}, respectively, they are considerably more negative for acyclic (**X**−**XII**) and cyclic (**XII** and **XIV**) siloxanes, −14 and −13 kJ mol^{-1}, respectively.

Table 2. Experimental (Exptl.) and Calculated (CBS-QB3, W1X-1, and W2) Gas-Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}) of Silicon Compounds Considered in This Work[a]

molecule	$\Delta_f H^\circ$ 298 K			
	exptl.	CBS-QB3	W1X-1	W2
SiH_4	34.3 ± 1.2	27.0	35.9	
Si_2H_6	79.9 ± 1.5	74.2	81.1	
Si_3H_6	120.9 ± 4.4	113.7	120.4	
SiH_3Me	−29.1 ± 4.0	−27.6	−23.8	
SiH_2Me_2	−94.7 ± 4.0	−85.1	−85.9	
$SiHMe_3$	−163.4 ± 4.0	−145.2	−149.9	
$SiMe_4$	−233.2 ± 3.2	−207.4	−215.0	−212.8
Si_2Me_6	−303.7 ± 5.5	−267.3	−280.3	−277.0
$Si(OH)_4$	−1351.3 ± 1.7	−1344.2	−1341.7	
$SiMe_3(OH)$	−500.0 ± 3.0	−483.4	−488.2	
$Si(OEt)_4$	−1356.0 ± 6.0	−1345.7	−1337.7	−1331.4
$O(SiMe_3)_2$	−777.4 ± 6.0	−756.2	−760.0	−761.0
$NH(SiMe_3)_2$	−477.0 ± 5.0	−454.0	−472.0	−460.8

[a]Experimental data are taken from the two most recent compilations by Becerra and Walsh.[18,19]

Closer inspection of data in Table 1 reveals that the observed trends originate from systematic differences between W1X-1 and CBS-QB3 results. For example, the CBS-QB3 enthalpy of formation of the parent silane SiH_4 is less than the corresponding W1X-1 prediction, and each successive substitution by alkyl, alkenyl, or aryl groups affects the difference in a very consistent way. Thus, the CBS-QB3 enthalpies become greater than W1X-1 values for monosilanes with two or more substituents, and the differences are notable for tetrasubstituted species and for systems with more than one phenyl substituent. Similarly, the CBS-QB3 enthalpies for siloxanes with one or two silyl or fluorosilyl substituents are markedly lower than the corresponding W1X-1 values, and the prevalence of this type of compounds in groups **X** and **XI** manifests itself in the very negative MSD value.

Having established that there are systematic differences between the two sets of computational standard gas-phase enthalpies of formation, an important question to ask is which method, W1X-1 or CBS-QB3, is more trustworthy, and how do the calculated numbers compare with their experimental counterparts. From a purely theoretical viewpoint, W1X-1 is more robust and advanced than CBS-QB3 and should be preferred. This is also borne out by comparing the 1/2/3σ confidence intervals of CBS-QB3 (determined against the active thermochemical tables), ±7/±14/±21 kJ mol^{-1},[70] to those of W1X-1 (estimated from the MAD with respect to G2 and G3 data sets), ±3/±6/±9 kJ mol^{-1}.[26] Since both CBS-QB3 and W1X-1 contain empirical parameters that are potential sources of systematic error, we used the parameter-free W2 method as a very high-level reference in cases where significant (>3σ) discrepancies between calculated and experimental enthalpies were observed. Even though the confidence intervals of W2 have not been determined, its MAD with respect to G2 enthalpies of formation is lower than the average 2σ uncertainty of experimental values in the reference data set.[4,59]

As discussed in the Introduction section, reliably determined gas-phase standard enthalpies of formation for silicon compounds are few and far between, which is reflected in the reference data available for comparison with the values calculated herein.[17−19] Well-established experimental values exist only for 13 compounds in Chart 1 (Table 2; reported uncertainties correspond to 2σ confidence intervals). The two most recent compilations by Becerra and Walsh contain the citations to the original work as well as an in-depth discussion of the reliability of the data and why particular values are recommended over others.[18,19] Becerra and Walsh have also determined enthalpies of formation via semi-empirical means (bond and group additivity considerations as well as electronegativity correlations) that can also be used for comparison.[17−19] These are of lesser significance than first-hand (calorimetric) measurements, for which reason we have explicitly pointed out their use in the following discussion. The same is also true for the data reported by Voronkov et al.[20−25] that have consistently been flagged dubious by Becerra and Walsh through comparisons with other reference data or with estimates based on reasonable chemical expectations.[17−19]

Comparison of computational data for parent mono- and polysilanes with the recommended experimental values shows that the W1X-1-calculated enthalpies of formation for silane SiH_4, disilane Si_2H_6, and trisilane Si_3H_8 (35.9, 81.1, and 120.4 kJ mol^{-1}, respectively) are in excellent agreement with calorimetric data, 34.3 ± 1.2, 79.9 ± 1.5, and 120.9 ± 4.4 kJ mol^{-1}, respectively. In comparison, the CBS-QB3 calculated enthalpies for the same set (27.0, 74.2, and 113.7 kJ mol^{-1}, respectively) are all less endothermic and further away from the experimental values.

The well-established experimental enthalpies of formation for the methylsilane series SiH_3Me, SiH_2Me_2, $SiHMe_3$, and $SiMe_4$ are −29.1 ± 4.0, −94.7 ± 4.0, −163.4 ± 4.0, and −233.2 ± 3.2 kJ mol^{-1}, respectively. Additionally, Voronkov et al. have reported a value of −229.0 ± 3.0 kJ mol^{-1} for $SiMe_4$,[20]

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in good harmony with the earlier calorimetric measurement. A comparison of these data with W1X-1 (−23.8, −85.9, −149.9, and −215.0 kJ mol^{-1}, respectively) and CBS-QB3 (−27.6, −85.1, −145.2, and −207.4 kJ mol, respectively) values shows that the difference between calculated and experimental values increases with the number of methyl groups. In fact, both W1X-1 and CBS-QB3 values for $SiMe_4$ are statistically (3σ) different than the experimental result. The W2 method gives −212.8 kJ mol^{-1} for the enthalpy of formation of $SiMe_4$, in excellent agreement with the W1X-1 value. For this reason, we conclude that the experimental enthalpy of formation of $SiMe_4$ is too exothermic. Furthermore, since the experimental enthalpies of formation for SiH_3Me, SiH_2Me_2, and $SiHMe_3$ are based on data from methyl redistribution reactions and employ the calorimetric enthalpy of formation of $SiMe_4$ as a common reference,[71] their values should also be adjusted accordingly.

The recommended enthalpy of formation of hexamethyldisilane Si_2Me_6, −303.7 ± 5.5 kJ mol^{-1}, has been determined using solution calorimetry. This value is statistically (3σ) different from those obtained with W1X-1 and CBS-QB3 methods (−280.3 and −267.3 kJ mol^{-1}, respectively). For comparison, the W2 method yields −277.0 kJ mol^{-1}, in excellent agreement with W1X-1. Consequently, the experimental enthalpy of formation of Si_2Me_6 is almost certainly too exothermic.

Voronkov et al. have reported a value of −297.0 ± 5.0 kJ mol^{-1} for the enthalpy of formation of tetraethylsilane $SiEt_4$.[20] This result is significantly more exothermic than the values calculated with W1X-1 and CBS-QB3 (−251.9 and −238.8 kJ mol^{-1}, respectively) and clearly in error. In contrast, Becerra and Walsh have recently suggested a value of −269 kJ mol^{-1} for this quantity based on group additivity estimates,[19] in much better agreement with the calculated enthalpies and the W1X-1 value in particular. In a similar fashion, the estimated enthalpies of formation for the ethylsilane series SiH_3Et, SiH_2Et_2, and $SiHEt_3$ are −46, −129, and −214 kJ mol^{-1}, respectively.[18] However, these are based on an older methyl-to-ethyl substitution replacement enthalpy, $\Delta\Delta$(Me/Et) = −17 kJ mol^{-1}, whereas a revised value of −9 kJ mol^{-1} was used to derive the estimate for $SiEt_4$.[19] Correcting the ethylsilane data with the revised $\Delta\Delta$(Me/Et) value, which, in fact, matches perfectly with the difference between the W1X-1 enthalpies for SiH_3Me and SiH_3Et (Table 1), gives −38, −113, and −190 kJ mol^{-1} for SiH_3Et, SiH_2Et_2, and $SiHEt_3$, respectively. Considering the large 2σ uncertainty (±16 kJ mol^{-1}) associated with these estimations, the agreement with our W1X-1 values for SiH_3Et and SiH_2Et_2 (−32.8 and −103.7 kJ mol^{-1}, respectively) is very good.

Voronkov et al. have quoted −191.0 ± 5.0 kJ mol^{-1} for the enthalpy of formation of trimethylvinylsilane $SiMe_3Vi$.[20] This value has been heavily criticized by Walsh and Becerra,[17,18] and both W1X-1 and CBS-QB3 results obtained herein (−96.5 and −87.6 kJ mol^{-1}, respectively) clearly support these concerns. A revised value of −125 kJ mol^{-1} has been proposed by Becerra and Walsh based on hydrogenation enthalpies and isodesmic reaction data.[18] Even though this result is in better agreement with the calculated data than the value reported by Voronkov et al., the estimated enthalpy is, nevertheless, too exothermic based on our calculated values. Becerra and Walsh have also derived a recommended value for the enthalpy of formation of the parent vinylsilane SiH_3Vi, 87.0 kJ mol^{-1},[19] that is in reasonably good agreement with our W1X-1 and CBS-QB3 enthalpies (96.9 and 94.3 kJ mol^{-1}, respectively). We note that if the estimate of Becerra and Walsh for SiH_3Vi is corrected with $\Delta\Delta$(H/Me) = −63 kJ mol^{-1}, determined from our data for the vinylsilane series, the estimated enthalpy of formation for $SiMe_3Vi$ becomes −102 kJ mol^{-1}, in good agreement with our calculations.

The benchmark enthalpies of formation reported for tetrahydroxysilane $Si(OH)_4$, trimethylsilanol $SiMe_3(OH)$, and tetraethoxysilane $Si(OEt)_4$ are −1351.3 ± 1.7, −500.0 ± 3.0, and −1356.0 ± 6.0 kJ mol^{-1}, respectively. Our W1X-1 (−1341.7, −488.2, and −1337.7 kJ mol^{-1}, respectively) and CBS-QB3 (−1344.2, −483.4, and −1345.7 kJ mol^{-1}, respectively) results are mostly in harmony with each other and in reasonable agreement with the experimental values. The only exception to the trend is tetraethoxysilane, for which the W1X-1 enthalpy hits the limits of the associated 3σ confidence intervals. The W2 enthalpy of $Si(OEt)_4$ is −1331.4 kJ mol^{-1}, and, therefore, in better agreement with the W1X-1 value than with experimental data, suggesting that the latter should be slightly adjusted. Voronkov et al. have reported an even less exothermic enthalpy of formation for this compound, −1315.0 ± 6.0 kJ mol^{-1}, that is clearly erroneous, but the value they quote for trimethoxymethylsilane $SiMe(OMe)_3$, −944.0 ± 5.0 kJ mol^{-1}, is in very good agreement with our W1X-1 and CBS-QB3 results (−948.6 and −957.6 kJ mol^{-1}, respectively).[20]

Using group additivity approaches, Becerra and Walsh have derived enthalpies of formation of −259 and −1220 kJ mol^{-1} for methoxysilane $SiH_3(OMe)$ and tetramethoxysilane $Si(OMe)_4$, respectively.[19] These are in good agreement with our CBS-QB3 data (−253.7 and −1209.9 kJ mol^{-1}, respectively) but differ more from the values calculated with W1X-1 (−245.8 and −1195.9 kJ mol^{-1}, respectively). The match between group additivity estimates and CBS-QB3 data is expected to be only fortuitous, and the calculated W1X-1 values should be considered the most trustworthy of the three. An additional reference point is provided by Voronkov et al., who quote −1180.0 ± 5.0 kJ mol^{-1} for the enthalpy of formation of tetramethoxysilane,[20] in reasonable agreement with our W1X-1 result.

Only a single well-established (bomb calorimetry) enthalpy of formation has been reported for siloxanes considered in this work: −777.4 ± 6.0 kJ mol^{-1} for hexamethyldisiloxane $O(SiMe_3)_2$. A reassessment of this value by Voronkov et al. led to a matching result of −778.6 ± 4.0 kJ mol^{-1}.[22] The calculated W1X-1 and CBS-QB3 enthalpies of formation are both less exothermic (−760.0 and −756.2 kJ mol^{-1}, respectively), and the W1X-1 value is only barely inside the associated 3σ confidence intervals. A reassessment of the enthalpy of formation of hexamethyldisiloxane with the W2 method yields −761.0 kJ mol^{-1}, in excellent agreement with the W1X-1 value. This suggests that the experimental data are most likely slightly too exothermic.

Voronkov et al. have also determined the standard enthalpy of formation of hexamethylcyclotrisiloxane $(OSiMe_2)_3$, −1568.0 ± 10.0 kJ mol^{-1}.[24] Their result is almost 100 kJ mol^{-1} less exothermic than our W1X-1 and CBS-QB3 enthalpies that are in excellent agreement with each other (−1648.3 and −1653.8 kJ mol^{-1}, respectively), casting further doubt over the experimental work of Voronkov et al.

The last compound to consider is hexamethyldisilazane $NH(SiMe_3)_2$, for which the recommended enthalpy of formation, −477.0 ± 5.0 kJ mol^{-1}, is based on solution calorimetry. A more recent investigation was performed by

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Voronkov et al., leading to a slightly less exothermic value, −450.8 ± 10.0 kJ mol^{-1},[25] but with much larger uncertainty. Interestingly, our calculated W1X-1 enthalpy (−472.0 kJ mol^{-1}) is a good match with the result from solution calorimetry, whereas the CBS-QB3 value (−454.0 kJ mol^{-1}) agrees nicely with the work of Voronkov et al. Consequently, we used the W2 method as an adjudicator, and the result, −460.8 kJ mol^{-1}, agrees slightly better with the CBS-QB3 data, casting some doubt over the use of solution calorimetry result as the well-established experimental value.

Considered as a whole, the standard gas-phase enthalpies of formation calculated with the W1X-1 and W2 methods are consistently in better agreement with experimental data than those obtained with the CBS-QB3 approach. Consequently, systematic differences between W1X-1 and CBS-QB3 can be attributed to inadequate treatment of electron correlation effects in the latter that become more prominent with increasing molecular size. This is in stark contrast to our previous study on phosphines and phosphine oxides,[31] in which case W1X-1 and CBS-QB3 showed much more uniform performance, albeit for a more limited set of compounds with less variety in the employed substituents. W1X-1 enthalpies are, therefore, considered superior to CBS-QB3 results and used exclusively in the remaining parts of the analysis and discussion. Furthermore, in those cases where W1X-1 and experimental values differ more than the associated 3σ intervals, the very high-level W2 method yields values in better agreement with W1X-1. This allows us to conclude that the experimental standard gas-phase enthalpies of formation of $SiMe_4$ and Si_2Me_6 are too exothermic, while those of $Si(OEt)_4$, $O(SiMe_3)_2$, and $NH(SiMe_3)_2$ are borderline cases and could also require adjustment.

Comparison of Calculated Gas-Phase Standard Enthalpies of Formation with Prior Computational Data. To the best of our knowledge, the works of Burcat and Goos[28] and Janbazi et al.[29,30] represent the most recent large-scale attempts to calculate thermochemical parameters of organosilicon compounds using computational methods. Their data have been obtained with the G3 and G4 composite methods, respectively, whose expected accuracy is in between those of W1X-1 and CBS-QB3, although closer to the former than the latter.[70] The earlier work of Feller and Dixon,[27] while not nearly as comprehensive, needs to be mentioned in this context because it reports very high-level CCSD(T)/CBS benchmark data for nine small silicon compounds, including SiH_4 and Si_2H_6. We stress that the abovementioned papers are not by any means the only ones dealing with computational thermochemistry of organosilicon compounds and many other authors have touched different aspects of the field over the years. Regardless, the efforts by Burcat and Goos[28] and Janbazi et al.[29,30] are the most comprehensive available and cover a large part of the species that had been investigated prior to their work. For a review of pre-2015 computational data on the field, the papers by Burcat and Goos[28] and Becerra and Walsh[19] are excellent references.

A comparison of computational data for Si_xH_y systems shows that our W1X-1 values for SiH_4, Si_2H_6, and Si_3H_8 (35.9, 81.1, and 120.4 kJ mol^{-1}, respectively) are identical, within the accuracy of the methods, to prior results of Feller and Dixon and Burcat and Goos after adjusting the latter values to the same temperature (298.15 K) and employing the same atomic reference values including spin−orbit corrections (adjusted values 33.0, 76.3, and 122.7 kJ mol^{-1} for SiH_4,[27] Si_2H_6,[27] and Si_3H_8,[28] respectively). The G4 enthalpies of formation given by Janbazi et al.[29] for Si_2H_6 and Si_3H_8 agree with the above values after similar adjustments (78.8 and 118.4 kJ mol^{-1}, respectively). Interestingly, the same does not hold for the methylsilane series, for which the adjusted data from Janbazi et al.[29] (−26.2, −87.3, −160.0, and −233.6 kJ mol^{-1} for SiH_3Me, SiH_2Me_2, $SiHMe_3$, and $SiMe_4$, respectively) show a gradually increasing deviation from our W1X-1 values (−23.8, −85.9, −149.9, and −215.0 kJ mol^{-1}, respectively). For comparison, the adjusted G3 values of Burcat and Goos[28] for $SiHMe_3$ and $SiMe_4$ are −157.7 and −223.8 kJ mol^{-1}, respectively. Most surprising are, however, the CBS-QB3 values of Janbazi et al.[29] that are, after adjustments, 69.2, 107.3, and −213.8 kJ mol^{-1} for Si_2H_6, Si_3H_8, and $SiMe_4$, respectively, and differ from the values reported by us (74.2, 113.7, and −207.4 kJ mol^{-1}), even though the computational method used is identical. It is unfortunate that no more details of their work are provided by Janbazi et al. as this would have allowed us to trace the origin of this discrepancy.

Even more perplexing is the observation that the G4 data reported by Janbazi et al.[30] for silanols and alkoxysilanes in their second paper are in much better agreement with our values in Table 1 than what was seen in the case of simple (alkyl)silanes. This is surprising, given that the same composite method and atomization approach were used in both studies. Thus, we have no significant reservations about the enthalpies of formation reported in the follow-up work of Janbazi et al.[30] saved for the fact that their reference value for SiH_3OH, −285.2 kJ mol^{-1}, can be slightly too exothermic (cf. W1X-1 value of −280.1 kJ mol^{-1}). If this turns out to be the case, a significant systematic error could occur when the value is combined with large stoichiometric coefficients used to calculate the standard enthalpies of formation via isodesmic reactions. We will return to the computational results of Janbazi et al. when discussing the group additivity contributions they have determined based on the reported enthalpies.

Benson Thermochemical Group Contributions for Silicon and Their Use in Assessing the Reliability of Experimental Data Reported by Voronkov et al. Group additivity contributions allow for fast and accurate estimation of chemical properties of many organic compounds. In this work, we used the calculated W1X-1 thermochemical data in Table 1 to derive Benson group contributions for 60 silicon-based groups and group pairs given in Tables 3 and 4, respectively. The convention by Holmes and Aubry was adopted, where all values are rounded to the nearest integer to underline the internal character of group contribution methods to estimate, rather than calculate, thermochemical parameters.[13,14] In the case of aryl-substituted species, Benson groups always occur in pairs, which prevents the easy assignment of unambiguous values for individual groups.[72] These can be derived by assigning arbitrary reference values for key groups, such as the group $C_B-(C_B)_2(Si)$ discussed herein. While this convention has been adopted by some authors, including Benson in his later works,[15] we chose to report group pair contributions following the practice adopted in our previous work.[31]

As discussed earlier, Becerra and Walsh have derived group contributions for silicon-based Benson groups and used them extensively in their work. Comparison of our W1X-1 data in Table 3 with their values shows good agreement with groups $Si-(C)(H)_3$, $O-(C)(Si)$, $Si-(C)_2(O)_2$, and $Si-(C)(O)_3$ (former values 14, −247, −62, and −61 kJ mol^{-1},

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Table 3. Thermochemical Benson Group Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), Entropies (S°_{298K}, J K^{-1} mol^{-1}), and Heat Capacities (C_p, J K^{-1} mol^{-1}) Derived from the Results of W1X-1 Calculations

Benson group	$\Delta_f H^\circ$ 298 K	S° 298 K	C_p 298 K	C_p 500 K	C_p 1000 K
Si−(C)(H)$_3$	19	156	32	45	63
Si−(C$_D$)(H)$_3$	34	149	28	45	64
Si−(H)$_3$(O)	38	151	30	44	63
Si−(H)$_3$(Si)	41	152	35	49	68
Si−(C)$_2$(H)$_2$	−1	72	31	40	51
Si−(C$_D$)$_2$(H)$_2$	28	53	25	40	52
Si−(O)$_2$(H)$_2$	9	56	31	41	51
Si−(Si)$_2$(H)$_2$	38	68	36	46	59
Si−(C)(C$_D$)(H)$_2$	14	63	28	40	51
Si−(C)(H)$_2$(O)	10	63	30	39	50
Si−(C)(H)$_2$(Si)	25	69	34	43	55
Si−(C$_D$)(H)$_2$(O)	26	53	26	39	51
Si−(F)(H)$_2$(O)	−381	159	38	52	68
Si−(C)$_3$(H)	−23	−8	32	36	38
Si−(C$_D$)$_3$(H)	20	−34	21	34	40
Si−(H)(O)$_3$	−32	−34	36	39	40
Si−(C)$_2$(C$_D$)(H)	−9	−16	28	35	39
Si−(C)$_2$(H)(O)	−19	−12	32	36	38
Si−(C$_D$)$_2$(H)(O)	11	−38	25	36	40
Si−(F)$_2$(H)(O)	−810	178	47	60	72
Si−(C)(C$_D$)$_2$(H)	5	−26	26	36	40
Si−(C)(H)(O)$_2$	−24	−26	32	37	39
Si−(C$_D$)(H)(O)$_2$	−7	−35	27	35	39
Si−(F)(H)(O)$_2$	−422	71	43	52	58
Si−(C)$_4$[a]	−46	−85	35	33	26
Si−(C)$_3$(O)[a]	−46	−85	35	33	26
Si−(C)$_3$(C$_D$)	−32	−87	30	32	26
Si−(C)$_3$(Si)	−13	−86	36	35	30
Si−(C)$_2$(C$_D$)$_2$	−19	−106	27	31	27
Si−(C)$_2$(O)$_2$	−55	−104	35	33	27
Si−(C$_D$)$_2$(O)$_2$	−23	−124	32	39	35
Si−(C)(C$_D$)$_3$	−6	−116	24	31	28
Si−(C)(O)$_3$	−59	−108	36	35	29
Si−(C)(C$_D$)(O)$_2$	−38	−111	28	31	26
Si−(F)$_3$(O)	−1224	214	59	71	78
Si−(F)$_2$(O)$_2$	−842	87	50	57	60
Si−(O)$_4$	−70	−132	43	38	30
C−(C)(H)$_2$(Si)	−9	34	22	32	50
C−(C)$_2$(H)(Si)	17	−59	19	28	39
O−(H)(Si)	−318	117	14	22	29
O−(C)(Si)	−240	39	5	9	16
O−(Si)$_2$	−416	38	10	17	26
ring strain, 6-membered ring	21	87	−5	−3	−3
ring strain, 8-membered ring	4	104	4	5	5

[a]Values for the group Si−(C)$_3$(O) have been fixed to those of Si−(C)$_4$.

respectively).[18] For all other Benson groups reported by Becerra and Walsh, such as Si−(C)$_4$/Si−(C)$_3$(O), C−(C)$_2$(H)(Si), and O−(Si)$_2$, the differences are much greater and even exceed 20 kJ mol^{-1} in some cases. This is entirely expected, considering the large differences seen between W1X-1-calculated enthalpies and the corresponding experimental values.

The group additivity contributions determined herein can also be compared with the work of Janbazi et al.[29,30] Unfortunately, this is not entirely justified as their data are based on Cohen's[73] revised formulation of Benson's approach.[9] Furthermore, different values for the groups C−(Si)(H)$_3$ and C−(C)(H)$_3$ have been chosen by Janbazi et al. to avoid "group-increment analogies".[29] Such a choice represents a significant step away from all Benson-type group additivity approaches that uniformly fix the contribution from a methyl group (except for its physical state) no matter what atom it is attached to.[9] In fact, the work of Janbazi et al. should not be considered an addition to Cohen's work, but it rather constitutes yet another branch to the ever-growing tree of group additivity approaches.

As discussed earlier, the inaccuracies in the computed enthalpies reported by Janbazi et al.[29,30] raise concerns over the group contribution values they have determined. In fact, the group contributions given by Janbazi et al. do not reproduce all G4-level enthalpies from which they are derived. For example, differences up to 8 kJ mol^{-1} are found in the methylsilane series, even though the fit to the reference data is claimed to have a maximum deviation of only 0.01 kJ mol^{-1}.[29] More significant is the fact that the values of some group contributions involving oxygen, such as Si−(O)$_4$ and Si−(C)(O)$_3$, differ considerably, up to 40 kJ mol^{-1}, between our data and theirs.[30] We note that Janbazi et al. do not indicate fixing any of the group contributions involving Si−O bonds. This would allow for an infinite number of equally good fits to their data of which one is presented in the publication. It needs to be stressed that the individual group contributions carry no physical meaning and pre-fixed values, while inherently arbitrary, are important to avoid linear dependencies.

The data reported in Tables 3 and 4 allow for a more accurate estimation of enthalpies of formation for a variety of organosilicon species than has been possible before. In this context, we chose to employ the established values, together with literature values for carbon-based groups,[10,11] to estimate the standard enthalpies of formation of organosilicon species examined experimentally by Voronkov el al.[20−25] We have already concluded that their data appear suspicious when compared with the W1X-1 (and W2) enthalpies of formation calculated herein. However, such comparisons could only be made for a handful of compounds as high-level calculations become prohibitively expensive with increasing molecular size. By using group contributions, standard enthalpies of formation can be easily estimated irrespective of molecular size, allowing comparisons not only between bigger systems but also between larger groups of compounds.

Considering tri- and tetrasubstituted alkylsilanes with alkyl chains longer than four carbon atoms, standard enthalpies of formation could be estimated for 22 species examined by Voronkov el al.[20] The results (Supporting Information) show that the values reported by Voronkov et al. are systematically around 40 kJ mol^{-1} more exothermic than those obtained using group additivity contributions. We feel confident that our values for groups C−(C)(H)$_2$(Si), Si−(C)$_4$, and Si−(C)$_3$(H) are reliable as they reproduce well all W1X-1 enthalpies for tri- and tetrasubstituted alkylsilanes in Table 1. Thus, the data by Voronkov et al. must contain an unknown source of systematic error, as initially suspected by Becerra and Walsh.[17−19] The published experimental details do not allow us to trace down the origin of the error, but one possible culprit is the standard enthalpy of formation of amorphous hydrated silica whose

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Table 4. Thermochemical Benson Group Pair Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), Entropies (S°_{298K}, J K^{-1} mol^{-1}), and Heat Capacities (C_p, J K^{-1} mol^{-1}) Derived from the Results of W1X-1 Calculations

Benson group	$\Delta_f H^\circ$ 298 K	S° 298 K	C_p 298 K	C_p 500 K	C_p 1000 K
Si−(C$_B$)(H)$_3$ + C$_B$−(C$_B$)$_2$(Si)	56	104	35	58	83
Si−(C)(C$_B$)(H)$_2$ + C$_B$−(C$_B$)$_2$(Si)	36	37	39	57	74
Si−(C$_B$)(H)$_2$(O) + C$_B$−(C$_B$)$_2$(Si)	50	31	44	62	80
Si−(C$_B$)$_2$(H)$_2$ + C$_B$−(C$_B$)$_2$(Si)	72	−3	49	74	98
Si−(C)$_2$(C$_B$)(H) + C$_B$−(C$_B$)$_2$(Si)	13	−47	41	53	62
Si−(C$_B$)(C$_D$)$_2$(H) + C$_B$−(C$_B$)$_2$(Si)	41	−65	36	53	63
Si−(C$_B$)(H)(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)	14	−63	41	53	62
Si−(C)(C$_B$)(C$_D$)(H) + C$_B$−(C$_B$)$_2$(Si)	26	−60	37	52	62
Si−(C)(C$_B$)(H)(O) + C$_B$−(C$_B$)$_2$(Si)	18	−53	40	53	62
Si−(C)$_3$(C$_B$) + C$_B$−(C$_B$)$_2$(Si)	−11	−118	44	50	50
Si−(C)$_2$(C$_B$)$_2$ + C$_B$−(C$_B$)$_2$(Si)	22	−167	55	68	73
Si−(C$_B$)$_2$(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)	14	−182	52	66	73
Si−(C)$_2$(C$_B$)(C$_D$) + C$_B$−(C$_B$)$_2$(Si)	2	−135	40	49	50
Si−(C)(C$_B$)(C$_D$)$_2$ + C$_B$−(C$_B$)$_2$(Si)	14	−147	38	50	51
Si−(C)(C$_B$)(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)	−19	−143	45	52	53
Si−(C$_B$)(C$_D$)(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)	−4	−154	55	70	74
2 Si−(C)$_3$(N) + N−(H)(Si)	−218	−134	93	98	96

value is dependent on the exact physical state after combustion. In fact, this problem has been comprehensively studied by Voronkov et al., and the value they use in their work, −939.39 ± 0.52 kJ mol^{-1}, stands out from all literature references by being the most exothermic.[74] Even though an adjustment to this value would make the errors much smaller in the current case, they would, in general, become greater for many other compound classes examined by Voronkov et al. (see below). We therefore conclude that either the exact physical state of amorphous hydrated silica is slightly different for each compound class investigated, which could well be the case, or the experimental data by Voronkov el al. contain more than once source of error.

In the case of longer-chain alkoxysilanes and phenyl-substituted cyclosiloxanes investigated by Voronkov el al.,[20,24] we found in total 10 compounds for which enthalpies of formation could be estimated using group contributions in Tables 3 and 4 (Supporting Information). For these compounds, the data show no indication of a similar systematic error as seen above, and the differences between the two sets of numbers vary both in sign and in magnitude. However, the absolute differences are smaller for alkoxysilanes than for cyclosiloxanes, and differences much greater than 100 kJ mol^{-1} are seen for cyclosiloxanes with six or eight phenyl groups. It is impossible to assess the origin of this discrepancy with certainty as there are no other experimental data available for comparison and our estimate of the enthalpy contribution associated with the group pair Si−(C$_B$)$_2$(O)$_2$ + C$_B$−(C$_B$)$_2$(Si) is based on a single calculated value due to the computational cost associated with these calculations. We therefore conclude that the experimental data for simple alkoxysilanes published by Voronkov et al.[20] appear to be of similar quality to many other experimental reports on organosilicon thermochemistry, but there exists a high possibility that the data for cyclosiloxanes are significantly in error.[24]

As a last test, we investigated trimethoxy- and triethoxysilanes with thioether substituents. Voronkov et al. have reported data for 15 compounds of this class,[22] but only 6 of them can be represented with the Benson groups considered herein and those found in the literature. The results (Supporting Information) are rather remarkable as the differences between experimental and estimated standard enthalpies of formation are less than the associated 3σ confidence intervals in all cases. Consequently, for this particular set of compounds, the data reported by Voronkov et al. are uniformly consistent with our estimations, although the number of compounds to be considered is rather small. It is unfortunately impossible to assess whether the data are inherently better than those of, for example, alkylsilanes or if the better match with our estimates is entirely fortuitous.

■ CONCLUSIONS

In this work, we established a comprehensive high-accuracy ab initio thermochemical benchmark database for 159 organosilicon compounds using the composite W1X-1 method. The results were compared to W2 level benchmark values and extant experimental data, as well as to prior computational values. The calculated results were also used to derive group additivity contributions for standard gas-phase enthalpy of formation, $\Delta_f H^\circ_{298K}$, entropy, S°_{298K}, and heat capacity, C_p, for 60 Benson groups and group pairs involving silicon that can, in turn, be employed in estimating accurate thermochemical parameters for compounds beyond the limitations imposed by the scaling of the W1X-1 method with respect to molecular size.

The most important results of this work can be summarized as follows:

(i) High-level W1X-1 (and W2) results imply that the experimental standard enthalpies of formation of organosilicon compounds need to be treated with caution, irrespective of their source. As a general trend, when the differences between calculated and experimental enthalpies are observed, experimental values are systematically more exothermic than theoretical predictions. As pointed out in virtually every description of calorimetric analysis of organosilicon compounds, there are numerous possible sources of error in a single experiment and even the most comprehensive studies are not immune to errors that are hard to find and even more difficult to fix. Furthermore, experimental enthalpies of formation can be interdependent, such as

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those of the methylsilane series, allowing an error in a single value to easily propagate to many others.

(ii) The vast experimental data set of Voronkov et al. is a double-edged sword. On one hand, it contains results, such as the enthalpies of formation of alkylsilanes, which were found to contain a significant systematic error, as initially suspected by Becerra and Walsh. On the other hand, the values reported by Voronkov et al. for alkoxysilanes appear to be no more in error than the results quoted by other authors. The obvious problem is how to differentiate between the two alternatives, and there appears to be no easy answer to this question. Thus, unless the data reported by Voronkov et al. are validated by an independent study, preferably by experimental means, we recommend that they continue to be flagged in thermochemical databases and treated with extreme caution.

(iii) Semi-empirical methods for the estimation of thermochemical properties of molecules are only as accurate as the underlying data used to derive them. The bond and group additivity contributions of Becerra and Walsh are based on experimental data for organosilicon compounds and were found to yield estimates with an accuracy of tens of kJ mol^{-1} at the best. Similarly, inaccuracies in the calculated enthalpies and problems associated with data fitting led to significant differences and incompatibilities between group contributions reported by Janbazi et al. and those from our approach. For these reasons, we consider the W1X-1-based group and group pair contributions reported herein the most accurate and recommend their use in all estimations of thermochemical properties of organosilicon species using Benson's methodology. In the case of Cohen's data sets, the values reported herein can be easily converted to comply with the revised parameterization. The W1X-1 data presented in this work also showed that even bond additivity approaches work well for the simplest of cases, for example, for the SiX_nY_{4-n} series, but only if the required substituent replacement enthalpies are determined from accurate enthalpy data.

As a last note, we join Becerra and Walsh and stress the importance of obtaining accurate thermochemical data on chemical compounds and organo-main group species in particular. Since a large-scale renaissance of calorimetry seems unlikely, partly due to limited funding opportunities available for such research, the role played by high-level ab initio theoretical methods, such as W1X-1, in this quest will be crucial. In this respect, we note that the W1X-1 method is currently only able to treat molecules with atoms from the first three rows of the periodic table, that is, up to argon. An extension of this approach to heavier main-group elements, such as germanium and bromine, is a highly desirable objective and currently under development in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c09980.

Calculated total energies and energy corrections, symmetry numbers for correction of optical isomerism and internal and external symmetries, and estimated standard enthalpies of formation (PDF)

Optimized molecular coordinates (XYZ)

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III

COMPUTATIONAL THERMOCHEMISTRY: EXTENSION OF BENSON GROUP ADDITIVITY APPROACH TO ORGANOBORON COMPOUNDS AND RELIABLE PREDICTIONS OF THEIR THERMOCHEMICAL PROPERTIES

by

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Computational thermochemistry: extension of Benson group additivity approach to organoboron compounds and reliable predictions of their thermochemical properties†

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High-level computational data for standard gas phase enthalpies of formation, entropies, and heat capacities are reported for 116 compounds of boron. A comparison of the results with extant experimental and computational benchmark values reveals important trends and clear outliers. Recommendations are made to revise some of the key quantities, such as the enthalpies of formation of orthoboric acid, trimethylthioborate, and triphenylborane, the last of which is found to be considerably in error. The uncertainties associated with the experimental values are found to exceed those of high-level calculations by a clear margin, prompting the redetermination of Benson group additivity contributions for boron-based groups on purely computational grounds. The applicability of the established group contribution values is demonstrated by estimating thermochemical data for large organoboron compounds that cannot be treated with high-level quantum chemical methods and comparing the results with existing experimental and computational values.

Introduction

The standard enthalpy (heat) of formation, $\Delta_f H$, describes the change in enthalpy when one mole of a given compound forms from its constituent elements in their standard states.[1] Since enthalpy is a state function, the enthalpy change of any reaction, $\Delta_r H^\circ$, can be calculated by taking the difference of the sum of standard enthalpies of formation of the products (i) and that of the reactants (j), with each value multiplied by its stoichiometric coefficient ν_n: $\Delta_r H^\circ = \sum \nu_i \Delta_f H_i^\circ - \sum \nu_j \Delta_f H_j^\circ$. While this approach works in principle for any reaction imaginable, it is in practise limited by the available experimental data. Specifically, the number of chemical compounds is currently counted in millions,[2] but the largest of thermochemical databases, such as the NIST Chemistry WebBook,[3] contain only a few thousand entries. For this reason, chemistry software for hazard analysis, heat balance calculations, and process simulation, such as RMG-Py,[4] CHETAH,[5] and JTHERGAS,[6] include modules that quickly estimate standard enthalpies of formation (and other thermochemical data) for molecules using their structures as the only input.

On-the-fly estimation of thermochemical properties of molecules typically employs group additivity methods that divide the species in question into well-defined and distinctive groups whose contributions to various physical properties are taken to be constant from one system to another.[7] The properties of a compound of interest are then obtained by summing up the tabulated values of all groups present in the molecule. In some cases, the results can be further adjusted by considering higher order (nonlinear) interactions between primary groups or specific structural features such as the presence of rings or different isomers. Although the additivity of molecular properties is not strictly fulfilled beyond atomic and molecular masses, empirical group additivity methods are able to estimate the thermodynamic properties of a wide range of molecular species with excellent accuracy and are superior to quantum chemical calculations in terms of speed.

The accuracy of group additivity approaches depends on the reliability of the reference values that have been used to derive the individual contributions and this is one of the Achilles' heels of the methodology. Even though standard enthalpies of formation of 'classical' organic species can often be estimated with high accuracy,[8,9] the same does not hold for more diverse chemical systems, like organo main group compounds, for which there are often not enough reliable thermochemical

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data.[10] For example, difficulties encountered in analysing the combustion products of organoboron compounds made reliable calorimetric work problematic prior to the advent of fluorine-containing combustion promoters.[11,12] Lately, the accumulation of thermochemical data has slowed down considerably, largely owing to the retirement of the generation of researchers familiar with calorimetry along with lack of interest in the younger generation and insufficient funding for this type of work.[13] This has spurred the development and use of high-accuracy quantum chemical methods, such as Feller-Peterson-Dixon (FPD),[14] Weizmann-*n* (W*n*),[15] and HEAT protocols,[16] whose accuracy is currently on-par with that of first-class calorimetric measurements and can be controlled by adjusting the underlying theoretical approximations.

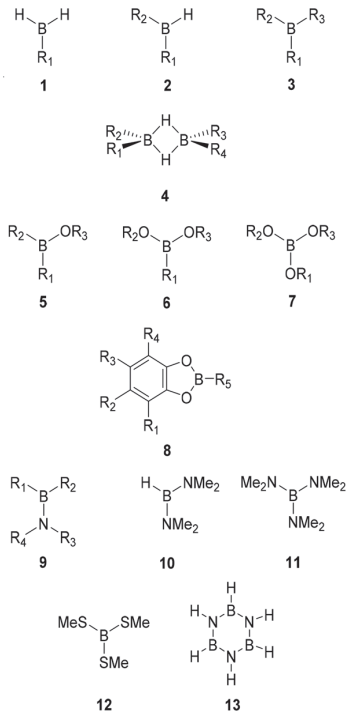
The current contribution has two main goals:

First, high-level composite quantum chemical methods are used to calculate the standard enthalpies of formation for 116 boron compounds. The results are compared with experimental reference values and very high-level FPD data, where available. The W1X-1 ansatz[17] used in the current work is a derivative of the Weizmann-1 protocol that can reach chemical accuracy, that is, mean absolute deviation (MAD) less than 4 kJ mol^{-1}, and is applicable to molecular systems with up to 20 non-hydrogen atoms when using server/workstation hardware. While high-level computational investigations of thermochemical properties of boron compounds have been performed before, our work is the first one using a large and diverse set of molecules with complex substituents. This allows, for example, an evaluation of the accuracy of literature data for large organoboron compounds, such as triphenylborane, for which several different experimental enthalpies of formation have been reported.

Second, boron-containing compounds have a plethora of applications in modern chemical industry. They are used as reagents in organic transformations,[18–21] components in materials for energy storage and conversion,[22–27] and as pharmaceuticals,[28–30] to name a few. Despite this, reliable data of their thermochemical properties are in many cases lacking and/or difficult to obtain by experimental means. At present, group additivity approaches offer no remedy to the problem as the only readily available compilation including boron is that of Benson and co-workers from 1969 and it is largely based on old calorimetric data using estimated quantities.[31] In contrast, the consistency of computational data reported herein allows the derivation of significantly more accurate group contributions for 52 Benson groups and group pairs involving boron. These values enable a straightforward extension of group additivity methods to boron-based compounds.

Computational details

Following our previous work,[32,33] the W1X-1 composite method[17] was employed to calculate the standard gas phase enthalpies of formation ($\Delta_f H°_{298K}$, kJ mol^{-1}), entropies ($S°_{298K}$, J K^{-1} mol^{-1}), and heat capacities (C_p, J K^{-1} mol^{-1}) for 116 boron compounds including 40 monoboranes (**1–3**), 7 diboranes (**4**), 15 borinic acid derivatives (**5**), 23 boronic acid derivatives (**6**), 11 boric acid derivatives (**7**), 11 catecholboranes (**8**), 7 aminoboranes (**9–11**), one thioborate (**12**), and borazine (**13**) with alkyl (Me = methyl, Et = ethyl, Pr = propyl, ^{i}Pr = isopropyl, Bu = butyl, ^{s}Bu = *sec*-butyl, ^{t}Bu = *tert*-butyl), alkenyl (Vi = vinyl, All = allyl), aryl (Ph = phenyl, *p*-Tol = *para*-tolyl) and/or halogen substituents. The size of the examined systems was limited by the scaling of the W1X-1 method and the available hardware (computing nodes with 14 TB SSD disk, 36 CPU cores and 1 TB memory) that allowed the treatment of molecules with up to *ca.* 20 heavy atoms. Given the high computational cost of the W1X-1 method, results from the less demanding and thereby significantly faster CBS-QB3 composite method were used for comparison.[34] In both methods, the computational bottleneck is a conventional CCSD(T) calculation, but the biggest basis set used in W1X-1 is approximately twice the size of that in CBS-QB3. Consequently, the CBS-QB3 method is roughly two orders of magnitude faster than W1X-1. However, as described in detail in below, the largest differences between the two methods are observed for the biggest of systems, and it is generally not recommended to substitute W1X-1 data with CBS-QB3 values.



All structure optimizations were performed with the Gaussian 16 program package.[35] Extensive conformational scans were carried out at the B3LYP[36–39]/cc-pV(T+d)Z[40,41] level of theory and only the lowest energy geometries were used as input for W1X-1 energy calculations. When applying the CBS-QB3 method, the geometries were reoptimized at the

B3LYP/6-311G(2d,d,p)[42,43] level of theory, as required by the composite protocol. For very high-level work, an ensemble of conformers having statistically significant populations at 298 K should be used for the calculation of standard enthalpies of formation instead of a single low-energy conformer. However, Bolzmann averaging is significant only when the conformational space is large and it is computationally very expensive to include at the W1X-1 level of theory. Furthermore, it has been shown that the resulting correction is similar (to a few kJ mol^{-1}) in magnitude but opposite in sign to the correction for low-frequency internal rotations, and they effectively cancel out.[44] Thus, both corrections should either be included or omitted, and the latter avenue was followed in this work. It should also be noted that neither CBS-QB3 or W1X-1 uses a dispersion correction during geometry optimization, which could lead to inferior results for systems in which these effects are important.

The CBS-QB3 method was used as implemented in Gaussian 16.[35] Single point runs performed with the Molpro 2019.2 program system[45–47] were used to calculate the W1X-1 energies as a sum of four different terms, namely $E_{\text{HF-CABS}}$, $E_{\Delta\text{CCSD-F12b}}$, $E_{\Delta(\text{T})}$, and $E_{(\text{C+R})}$, following the protocol of Chan and Radom.[17] The three non-relativistic components $E_{\text{HF-CABS}}$, $E_{\Delta\text{CCSD-F12b}}$, and $E_{\Delta(\text{T})}$ were extrapolated to the complete basis set (CBS) limit using cc-pVD/TZ-F12[48–51] (HF-CABS[52] and CCSD-F12b[53,54]) and aug′-cc-pV(D/T+d)Z[40,41] (CCSD(T))[55,56] basis sets and the extrapolation formula[57] $E_{\text{L}} = E_{\text{CBS}} + A_{\text{L}}^{-\alpha}$ where L is the cardinal number of the basis sets (that is, 2 or 3) and α is a method-dependent exponent (5, 3.6725, and 2.0436 for HF-CABS, CCSD-F12b, and CCSD(T), respectively).[17] The fourth energy component $E_{(\text{C+R})}$ is a combined core and scalar relativistic correlation term that was obtained as the difference of FC-MP2[58]/cc-pCVTZ[59,60] and DKH-MP2[61,62]/cc-pCVTZ[59,60] energies.

For the determination of standard enthalpies of formation, heat capacities, and entropies, the B3LYP level harmonic vibrational frequencies were scaled with 0.985 (W1X-1) or 0.990 (CBS-QB3). The calculation of entropies and heat capacities was carried out within the rigid rotor-harmonic oscillator approximation and treating rotation modes involving single bonds as hindered rotors using the procedure implemented in Gaussian 16.[35] A periodicity of 3 was used for all bonds to and within alkyl groups, whereas periodicity 2 was used for other single bonds. Symmetry numbers 3 and 2 were used for bonds with local C_3 and C_2 symmetries, respectively, while symmetry number 1 was used for all other bonds.

Standard gas phase enthalpies of formation were obtained using the atomization energy approach. The calculated atomic energies were corrected for spin–orbit (SO) coupling effects using the experimental values tabulated by Moore.[63] Reference values for the enthalpies of formation of gaseous atoms and thermal corrections for elements in their standard states were taken from NIST/JANAF Thermochemical Tables for elements H, C, N, O, F, and Cl.[64] For gaseous B, the uncertainty of the NIST/JANAF value, 560 ± 12 kJ mol^{-1}, is prohibitively large and there exits ample experimental[65,66] and computational[67–69] evidence that it should be revised upwards. To this end, we opted to use the value 570.3 ± 0.8 kJ mol^{-1} recommended by Karton and Martin based on very high-level theoretical calculations and experimental data for BF_3.[70]

The computed W1X-1 thermochemical parameters were used to derive Benson group contributions for 52 groups and group pairs containing boron. The contributions were determined by minimizing the squared differences between the computed thermochemical parameters and parameters calculated as sums of group contributions using a non-linear optimization algorithm COUENNE of the COIN-OR foundation[71] as implemented in OpenSolver.[72,73] Literature values reported by Domalski and Hearing[74,75] were used for all carbon groups, while some of the groups were required to be fixed to avoid linear dependencies. Following Benson's example,[31] the fixed group contributions are: E–(C)(H)$_3$≡C–(C)(H)$_3$ for any element E, B–(O)$_3$≡B–(S)$_3$≡B–(N)$_3$≡N–(C)$_3$, and B–(F)$_2$(C)≡B–(F)$_2$(C$_{\text{D}}$).

For the determination of enthalpy contributions, methyl repulsion correction terms of Domalski and Hearing were used for tertiary and quaternary carbon atoms, while *ortho*-corrections were employed in the case of adjacent fluorine atoms and hydroxyl groups in catecholboranes.[74,75] Steric crowding around boron atoms in diboranes was equated to what is known for substituted alkenes and a *cis*-correction term was used to describe repulsions between methyl groups.[74,75] Ring strain in the five-membered ring of catecholboranes was described with a single parameter that was optimized in the fitting procedure. Entropy contributions were corrected for optical isomerism ($R \ln n$, where n is the total number of stereoisomers) and for internal (σ_{int}) and external (σ_{ext}) symmetries ($-R \ln \sigma_{\text{tot}}$, where $\sigma_{\text{tot}} = \sigma_{\text{ext}}\Pi^{i}(\sigma_{\text{int}})_{i}$) (see ESI for details†).[31]

Results and discussion

Comparison of calculated gas phase standard enthalpies of formation of boron compounds with experimental and computational data

Before comparing the calculated W1X-1 and CBS-QB3 standard enthalpies of formation (Table 1) with experimental values and prior computational data (Table 2), an initial evaluation of the relative performance of the two methods is warranted. A detailed examination of the data in Table 1 shows that with only a few exceptions in boric acid derivatives and catecholboranes, the CBS-QB3 method predicts standard enthalpies of formation that are more endothermic than those obtained with the W1X-1 protocol. Even though the observed differences are well in line with the expected accuracy of the methods, gauged by the confidence intervals determined against large reference data sets (2σ values of ±14 and ±6 kJ mol^{-1} for CBS-QB3[76] and W1X-1,[17] respectively), the fact that the largest differences between the two methods are observed for the biggest of systems infers of systematic error. Previously,[32,33] we have ascribed this behaviour to inferior treatment of electron correlation effects in CBS-QB3 over W1X-1 that become more pro-

Table 1 Calculated gas phase standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}), entropies ($S°$ 298K, J K^{-1} mol^{-1}), and heat capacities (C_p, J K^{-1} mol^{-1}) of monoboranes **1–3**, diboranes **4**, borinic **5**, boronic **6**, and boric acid derivatives **7**, catecholboranes **8**, aminoboranes **9–11**, thioborane **12**, and borazine **13**

Molecule	Chemical formula[a]	$\Delta_f H°$ 298K W1X-1	$\Delta_f H°$ 298K CBS-QB3	$S°$ 298K W1X-1	C_p 298K W1X-1	C_p 500K W1X-1	C_p 1000K W1X-1
1a	BH_3	103.9	103.7	188.2	27.8	36.2	53.4
1b	BH_2Me	32.2	36.7	250.0	46.8	67.5	102.7
1c	BH_2Et	21.3	27.6	288.0	69.1	100.7	153.2
1d	BH_2Vi	135.3	141.4	265.2	56.4	86.1	128.1
1e	BH_2Pr	−0.7	7.6	322.1	91.4	135.4	204.6
1f	$BH_2{}^iPr$	3.2	10.8	312.9	93.8	138.2	205.5
1g	$BH_2{}^sBu$	−16.9	−7.8	345.9	115.0	174.2	259.2
1h	$BH_2{}^tBu$	−22.6	−14.7	339.8	118.5	177.1	261.0
1i	BH_2Ph	160.9	172.5	313.9	98.6	163.0	245.6
2a	$BHMe_2$	−39.7	−31.1	291.0	68.0	99.8	152.1
2b	BHEtMe	−50.4	−40.2	332.4	89.8	132.1	202.2
2c	BHMeVi	64.0	74.0	315.6	79.7	120.6	180.6
2d	BHMePh	91.8	106.5	364.6	122.2	196.4	292.8
2e	$BHEt_2$	−60.4	−48.7	354.9	113.2	166.6	253.4
2f	BHEtVi	53.7	65.2	345.0	100.1	151.5	227.4
2g	$BHVi_2$	166.9	178.3	317.4	90.2	138.2	203.3
2h	BHPhVi	195.0	210.8	377.3	132.1	213.2	318.4
2i	$BH{}^iPr_2$	−96.7	−83.5	417.0	161.5	238.6	356.7
2j	$BHPh_2$	229.8	249.3	425.1	176.4	292.5	435.3
3a	BMe_3	−109.6	−97.8	357.5	90.6	132.7	201.4
3b	$BEtMe_2$	−121.3	−108.0	375.6	114.0	166.4	252.1
3c	BMe_2Vi	−2.3	10.6	357.8	103.0	151.1	223.8
3d	BMe_2Ph	26.1	43.3	404.4	146.4	228.6	340.6
3e	BEtMePh	16.1	34.5	459.1	164.2	258.5	389.9
3f	$BMeVi_2$	105.4	119.5	378.6	114.4	167.5	245.0
3g	BMePhVi	133.7	151.9	426.2	159.0	246.2	362.3
3h	$BMePh_2$	163.3	184.5	469.9	200.8	326.4	485.5
3i	BF_2Me	−809.4	−806.1	296.3	56.6	79.9	111.8
3j	BEt_3	−143.3	−127.5	423.4	161.7	235.6	354.2
3k	$BEtVi_2$	96.3	112.1	392.7	138.1	204.7	300.9
3l	$BEtF_2$	−819.0	−814.8	327.8	78.7	112.5	162.0
3m	BVi_3	213.5	228.4	394.1	123.1	181.2	265.1
3n	$BPhVi_2$	242.1	260.9	431.9	171.8	268.9	391.8
3o	BPh_2Vi	268.4	289.9	480.5	213.6	346.3	512.9
3p	BF_2Vi	−695.8	−691.9	306.7	71.5	101.3	137.1
3q	$B{}^iPr_3$	−194.1	−177.9	503.5	235.0	349.2	515.4
3r	BBu_3	−274.6	−248.7	632.4	292.6	436.8	659.3
3s	BPh_3	293.3	317.3	517.2	256.4	422.9	630.5
3t	BF_3	−1134.6	−1133.9	254.9	42.7	55.1	67.7
3u	BCl_3	−404.3	−411.5	290.0	55.0	64.9	71.8
4a	B_2H_6	40.6	46.9	232.2	48.2	78.7	126.6
4b	B_2H_5Me	−16.8	−7.4	282.1	71.5	112.2	176.4
4c	1,1-$B_2H_4Me_2$	−76.6	−64.5	314.3	95.5	145.9	226.1
4d	1,2-*cis*-$B_2H_4Me_2$	−71.3	−59.0	314.2	94.0	144.7	225.8
4e	1,2-*trans*-$B_2H_4Me_2$	−72.1	−59.9	314.1	95.5	145.7	226.1
4f	$B_2H_3Me_3$	−129.2	−114.3	357.1	118.6	178.5	275.5
4g	$B_2H_2Me_4$	−184.3	−166.8	381.9	141.3	211.1	324.9
5a	BH_2OH	−274.0	−271.9	230.8	34.1	50.4	74.3
5b	$BH_2(OMe)$	−245.8	−246.0	269.8	51.9	78.5	123.1
5c	$BH_2(OEt)$	−280.2	−278.7	303.2	73.7	113.5	174.8
5d	$BH_2(OPh)$	−121.3	−115.8	344.5	112.8	181.0	265.7
5e	BHMe(OH)	−347.3	−341.5	274.2	55.9	83.4	123.9
5f	BHEt(OH)	−358.0	−351.2	307.9	78.5	116.5	174.3
5g	BHPh(OH)	−210.6	−199.7	345.1	112.0	181.5	266.3
5h	BHMe(OMe)	−318.0	−314.7	312.7	74.3	111.3	172.6
5i	BHEt(OMe)	−329.0	−324.8	342.9	96.5	148.1	229.9
5j	BHPh(OMe)	−182.0	−173.7	384.0	133.3	213.0	318.9
5k	$BMe_2(OH)$	−415.0	−406.3	317.8	77.4	116.1	173.7
5l	$BMe_2(OMe)$	−381.7	−375.7	357.7	99.1	146.0	219.7
5m	BEtMe(OH)	−427.2	−417.1	348.7	99.0	148.8	223.6
5n	BMePh(OH)	−278.2	−264.8	387.0	136.0	214.6	314.0
5o	BMePh(OMe)	−244.6	−234.1	430.8	154.3	238.7	356.7
6a	$BH(OH)_2$	−646.3	−642.5	256.7	48.1	70.5	97.1
6b	$BH(OMe)_2$	−579.8	−581.9	338.8	84.0	126.3	190.2

Table 1 *(Contd.)*

Molecule	Chemical formula[a]	$\Delta_f H°$ 298K W1X-1	$\Delta_f H°$ 298K CBS-QB3	$S°$ 298K W1X-1	C_p 298K W1X-1	C_p 500K W1X-1	C_p 1000K W1X-1
6c	$BH(^iPrO)_2$	−719.7	−716.7	462.1	179.9	268.3	394.7
6d	$BMe(OH)_2$	−713.6	−707.3	304.8	70.2	103.6	146.4
6e	BMe(OH)(OMe)	−680.0	−676.9	342.3	88.5	131.9	192.7
6f	$BMe(OMe)_2$	−646.1	−646.3	379.8	109.2	158.5	236.5
6g	BMe(OEt)(OMe)	−680.4	−679.2	411.7	130.5	195.2	290.6
6h	$BMe(OEt)_2$	−713.8	−711.3	444.5	153.4	230.7	342.0
6i	$BEt(OH)_2$	−724.8	−717.4	331.1	92.5	136.9	197.1
6j	BEt(OH)(OMe)	−690.9	−686.9	372.4	110.7	164.2	242.3
6k	$BEt(OMe)_2$	−656.5	−656.2	412.5	130.9	191.3	286.9
6l	$BVi(OH)_2$	−600.7	−593.7	316.5	86.8	124.4	166.5
6m	BVi(OH)(OMe)	−567.5	−563.6	362.5	100.4	148.7	214.0
6n	$BVi(OMe)_2$	−531.7	−531.1	399.9	121.9	175.2	257.8
6o	$B(All)(OH)_2$	−627.3	−618.2	349.5	106.2	154.9	219.4
6p	B(All)(OH)(OMe)	−594.2	−588.3	390.3	121.6	181.0	264.3
6q	$B(All)(OMe)_2$	−552.7	−550.2	436.1	142.8	208.6	308.7
6r	$BPh(OH)_2$	−572.6	−562.6	382.0	125.3	198.2	284.6
6s	BPh(OH)(OMe)	−539.8	−532.9	418.2	145.3	226.0	330.0
6t	$BPh(OMe)_2$	−497.6	−494.1	448.1	169.3	256.2	378.5
6u	$B(p\text{-Tol})(OH)_2$	−605.8	−594.8	420.3	147.1	230.1	334.3
6v	B(*p*-Tol)(OH)(OMe)	−572.9	−565.1	457.9	166.8	257.4	379.5
6w	$B(p\text{-Tol})(OMe)_2$	−530.4	−526.0	487.4	187.4	286.4	426.7
7a	$B(OH)_3$	−1002.1	−998.0	272.2	65.8	93.1	119.1
7b	$B(OH)_2(OMe)$	−967.6	−966.8	323.5	83.4	119.4	164.5
7c	$B(OH)_2(OPh)$	−842.9	−836.5	398.7	139.0	223.2	308.7
7d	$B(OH)(OMe)_2$	−933.1	−935.8	365.1	101.3	145.6	209.5
7e	B(OH)(OMe)(OPh)	−809.2	−806.4	442.8	160.7	245.4	350.9
7f	$B(OMe)_3$	−898.6	−905.4	396.4	119.1	173.0	255.9
7g	$B(OEt)(OMe)_2$	−932.7	−937.7	437.6	141.1	208.8	309.3
7h	$B(OMe)_2(OPh)$	−775.5	−776.5	484.2	179.0	272.2	396.2
7i	$B(OEt)_2(OMe)$	−966.8	−970.4	469.8	162.9	244.8	362.8
7j	$B(OMe)(OPh)_2$	−652.5	−648.5	559.8	243.0	376.5	539.9
7k	$B(OEt)_3$	−1000.8	−1003.0	492.8	184.9	281.1	416.0
8a	$C_6H_4O_2BH$	−409.1	−406.7	322.0	104.3	173.2	253.8
8b	$C_6H_4O_2BMe$	−482.9	−478.8	371.8	127.8	206.2	303.2
8c	$3\text{-}C_6H_3FO_2BMe$	−662.3	−662.6	390.4	140.1	217.2	310.5
8d	$4\text{-}C_6H_3FO_2BMe$	−673.1	−672.9	389.5	140.4	217.8	310.8
8e	$3,4\text{-}C_6H_2F_2O_2BMe$	−834.8	−840.8	409.4	152.7	228.3	317.8
8f	$3,5\text{-}C_6H_2F_2O_2BMe$	−849.7	−853.8	408.8	152.8	228.7	318.0
8g	$3,6\text{-}C_6H_2F_2O_2BMe$	−836.9	−843.5	408.5	152.6	228.2	317.8
8h	$4,5\text{-}C_6H_2F_2O_2BMe$	−845.2	−850.7	407.6	153.0	228.8	318.1
8i	$3,4,5\text{-}C_6H_2F_2O_2BMe$	−1004.3	−1014.1	428.7	165.4	239.3	325.1
8j	$3,4,6\text{-}C_6H_2F_2O_2BMe$	−1006.8	−1016.9	427.6	165.2	239.2	325.1
8k	$C_6F_4O_2BMe$	−1159.1	−1175.1	448.5	177.8	249.7	332.1
9a	BH_2NH_2	−81.9	−79.3	228.4	39.2	59.1	88.1
9b	BH_2NHMe	−72.6	−70.2	270.7	58.1	88.4	137.5
9c	BH_2NMe_2	−70.0	−72.6	293.4	81.6	123.6	189.5
9d	$BHMeNH_2$	−147.0	−140.5	275.8	62.2	92.5	137.8
9e	BMe_2NH_2	−211.0	−201.4	312.3	84.5	125.5	187.2
10	$BH(NMe_2)_2$	−160.2	−159.1	390.4	146.2	216.5	328.3
11	$B(NMe_2)_3$	−239.6	−241.5	461.0	215.3	315.6	469.4
12	$B(SMe)_3$	−199.1	−199.7	435.1	152.8	203.2	270.1
13	$B_3N_3H_6$	−495.7	−480.8	287.8	87.0	142.6	208.7

[a] Used abbreviations: Me = methyl, Et = ethyl, Pr = propyl, ^{i}Pr = isopropyl, Bu = butyl, ^{s}Bu = *sec*-butyl, ^{t}Bu = *tert*-butyl, Vi = vinyl, All = allyl, Ph = phenyl, *p*-Tol = *para*-tolyl.

nounced with increasing molecular size. However, since the W1X-1 method contains empirical parameters,[17] the extrapolation exponents α fitted to data for small molecules, it is possible that also W1X-1 results have larger than anticipated error as the size of the system in question grows.

As noted in the Introduction, experimentally determined thermochemical data for boron compounds are limited. Well-established standard enthalpies of formation exist only for nine species examined in the current work (Table 2) and many of these values are associated with large uncertainties (2σ confidence intervals). The scarcity of first-hand calorimetric data for boron compounds has led to the adoption of other means to arrive at the missing entities. For example, lacking direct measurements for many gaseous boron compounds, the vast compilation of Skinner[77] uses estimated quantities to calculate the standard enthalpy of formation for several systems, while

Table 2 Experimental (Exptl.) and calculated (FPD, W1X-1, and CBS-QB3) gas phase standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}) of selected boron compounds

Molecule	Exptl.	FPD	W1X-1	CBS-QB3
BH_3	106.7 ± 10.0[64]	102.1[82]	103.9	103.7
B_2H_6	41.0 ± 16.7[64]	39.5[81]	40.6	46.9
BF_3	−1136.6 ± 0.8[82]	−1135.5[82]	−1134.6	−1133.9
BCl_3	−403.0 ± 2.1[83]	−404.6[82]	−404.3	−411.5
BMe_3	−125.0 ± 22.0[85]	—	−109.6	−97.8
BEt_3	−160.7 ± 15.0[85]	—	−143.3	−127.5
$B(OH)_3$	−992.3 ± 2.5[64]	−1003.3[82]	−1002.1	−998.0
$B(SMe)_3$	−156.5 ± 2.5[90]	—	−199.1	−199.7
$B_3N_3H_6$	−510.0 ± 13.0[64]	−497.1[92]	−495.7	−480.8

other authors have taken advantage of the computer-analysed compilation of Pedley and Rylance from the 1970s to derive enthalpies of formation for boron compounds.[78] When compiling Table 2, we have carefully reviewed the existing literature and included experimental results that are backed up by ample amounts of data, are derived in the most straightforward manner, and/or do not rely on estimated ancillary data. Furthermore, most of the compounds in Table 2 are sufficiently small that there exist very high-level FPD benchmark values for comparison.

The NIST-JANAF standard enthalpies of formation of borane and diborane are 106.7 ± 10.0 and 41.0 ± 16.7 kJ mol^{-1}, respectively.[64] Of these, the value for borane is based on ion appearance potentials,[79] whereas the data for diborane is a weighted average of eight different experimental determinations. The compilation of Gurvich *et al.* quotes different numerical values for both borane and diborane, 88.0 ± 10.0 and 36.6 ± 2.0 kJ mol^{-1},[80] respectively, that are, however, identical with NIST-JANAF values (within 2σ) and in good agreement with our calculated W1X-1 (103.9 and 40.6 kJ mol^{-1}) and CBS-QB3 (103.7 and 46.9 kJ mol^{-1}) results. The FPD enthalpies of formation have been reported for both borane and diborane.[81,82] The value for borane, 102.1 kJ mol^{-1},[82] is based on the Karton Martin enthalpy of formation of gaseous boron atom,[70] whereas the value for diborane, 41.6 kJ mol^{-1},[81] needs to be adjusted by −2.1 kJ mol^{-1}, giving 39.5 kJ mol^{-1}. Both FPD values are in good agreement with experimental data and results of our calculations.

Experimental standard enthalpies of formation of boron trifluoride and trichloride, −1136.6 ± 0.8[83] and −403.0 ± 2.1 kJ mol^{-1},[84] respectively, have been determined using calorimetry. These values are statistically identical to those listed in the NIST-JANAF Thermochemical Tables[63] and in the compilation of Gurvich *et al.*[80] Our W1X-1 (−1134.6 and −404.3 kJ mol^{-1}) and CBS-QB3 (−1133.9 and −411.5 kJ mol^{-1}) results reproduce the experimental values for both boron trifluoride and trichloride, as is also the case for FPD data reported in the literature (−1135.5 and −404.6 kJ mol^{-1}).[82] Consequently, it is without a doubt that the standard enthalpies of formation quoted for these molecules in thermochemical databases have been determined to the highest precision.

Table 2 includes experimental standard enthalpies of formation for two alkylboranes, −125.0 ± 22.0 and −160.7 ± 15.0 kJ mol^{-1} for trimethyl- and triethylborane, respectively.[85] These values have been determined by combustion calorimetry. The associated uncertainties are very large in both cases, primarily because of the inability of the authors to accurately characterise the nature and thermodynamic states of combustion products. Unfortunately, there are no other experimental reports on the thermochemistry of these species and instead of very high-level FPD data, the published computational standard enthalpy of formation of trimethylborane, −107.9 kJ mol^{-1}, is based on isodesmic reactions modelled at the G3 (MP2) level.[86] For this reason, the W1X-1 results for trimethyl- and triethylborane (−109.6 and −143.3 kJ mol^{-1}, respectively) set a new high-level computational benchmark for both compounds. Our values are identical (within 2σ) with the experimental data, supporting the validity of latter within the limits of the assigned uncertainties.

The NIST-JANAF standard enthalpy of formation of orthoboric acid,[64] −992.3 ± 2.5 kJ mol^{-1}, is based on calorimetric[12,87] and vapour pressure data.[88] Our W1X-1 and CBS-QB3 results (−1002.1 and −998.0 kJ mol^{-1}, respectively) are more exothermic than the literature value and the W1X-1 prediction is not identical with it within 2σ confidence intervals. This species has also been subjected to the FPD treatment, yielding −1003.3 kJ mol^{-1} for its standard enthalpy of formation,[82] in harmony with our W1X-1 value. This allows us to conclude that the established experimental standard enthalpy of formation of orthoboric acid is slightly too endothermic and should be adjusted accordingly.

The experimental standard enthalpy of formation of trimethylthioborate has been determined *via* enthalpy of hydrolysis.[89] The reported value, −156.5 ± 2.5 kJ mol^{-1}, is significantly more endothermic than our computational W1X-1 and CBS-QB3 results (−199.1 and −199.7 kJ mol^{-1}, respectively) even when considering 3σ confidence intervals. The authors of the original experimental work already noted that thermal effects from the evolution of gaseous methanethiol were neglected in the analysis, which could account for some of the difference between the numbers. Furthermore, boron–sulphur bond energy calculated from the data for trimethylthioborate was found to be approximately 20 kJ mol^{-1} smaller than bond energies determined from experimental data for higher trialkylthioborates,[89] casting further doubt on the experimental enthalpy of formation of trimethylthioborate. Even though FPD benchmark result is not available for comparison, we are inclined to adjust the reference standard enthalpy of formation of trimethylthioborate to match the W1X-1 prediction.

The last experimental reference value to be considered is the standard enthalpy of formation of borazine, −510.0 ± 13.0 kJ mol^{-1}. This value is reported in the NIST-JANAF Thermochemical Tables[64] and is based on the original calorimetric determination of the enthalpy of combustion of borazine,[90] with minor adjustments to the ancillary values used in the derivation. For this molecule, our calculated W1X-1 and CBS-QB3 values (−495.7 and −480.8 kJ mol^{-1}, respectively)

deviate from each other by as much as 15 kJ mol^{-1}, though the difference is still within the combined 2σ confidence interval of the two methods. However, only the W1X-1 value is identical (within 2σ) with the experimental value. Interestingly, the FPD value reported for this species is −483.3 kJ mol^{-1},[91] in seemingly better agreement with our CBS-QB3 result, but a later technical report by the same author quotes −497.1 kJ mol^{-1} as the "recalculated heat of formation of borazine",[92] spot on with our W1X-1 prediction. Considering that the report adjusts all enthalpies given in the original publication by 4.6 kJ per mol per boron atom, a likely reason for the correction is the adoption of an updated standard enthalpy of formation for gaseous B from Karton and Martin.[70] The same reference value is also used by us and with this in mind we conclude that high-level computational predictions support the accuracy of the experimental standard enthalpy of formation of borazine within the reported confidence interval.

To summarize, the data in Table 2 shows that our W1X-1 results are in excellent agreement (within 1.5 kJ mol^{-1}) with FPD values, where available. Together with the extensive assessment of the performance of the W1X-1 method against G2 and G3/99 test sets by its developers, this result strongly supports the use of W1X-1 composite approach for the determination of standard enthalpies of formation of boron compounds, lending credence to the data in Table 1. Except for orthoboric acid and trimethylthioborate, high-level W1X-1 and FPD results uniformly imply that the experimental values given in Table 2 are accurate within the reported uncertainties. However, considering the consistency of the computational results and their much smaller error limits in comparison to experiments, we recommend that the calculated standard enthalpies of formation of borazine, borane, diborane, and trimethyl- and triethylborane are used in thermochemical work aiming to high-accuracy results. In the case of orthoboric acid, the literature value for its standard enthalpy of formation is slightly too endothermic and requires a minor revision. In contrast, the experimental standard enthalpy of formation of trimethylthioborate is considerably in error and the significantly more accurate W1X-1 prediction should be used in place of it.

Comparison of calculated gas phase standard enthalpies of formation of boron compounds with reference data used by Benson and co-workers

As noted above, many of the reference values reported by Skinner in his compilation[77] or in other works[93–97] take advantage of estimates to calculate the gas phase standard enthalpy of formation for several boron species. These data have also been used by Benson and co-workers to derive group contribution values for boron.[31] Of the various boron compounds that Benson and co-workers have considered in their analysis, around half are among the systems calculated herein (Table 1). In the following, we compare our high-level W1X-1 predictions for these molecules to the data used by Benson (Table 3).

The reference standard enthalpies of formation for trimetyl- and triethylborane used by Benson and co-workers, 122.4 ± 23.0 and −152.8 ± 10.5 kJ mol^{-1},[31,77] respectively, have equally large uncertainties as the calorimetric data discussed in the previous section. Consequently, the two sets of values are statistically identical within the given uncertainties and thereby in good agreement with our calculated W1X-1 results (−109.6 and −143.3 kJ mol^{-1}, respectively). The reference value quoted for tributylborane,[31,77] −283.3 ± 10.9 kJ mol^{-1}, has been derived by Skinner and takes use of an estimated enthalpy of vaporization. Despite this, the value is in good agreement with our calculated W1X-1 enthalpy (−274.6 kJ mol^{-1}) and can be considered accurate within the limits of the given confidence intervals.

Table 3 Reference (Ref.) and calculated (W1X-1) gas phase standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}) of selected boron compounds

Molecule	Ref.	W1X-1
BMe_3	−122.4 ± 23.0[77]	−109.6
BEt_3	−152.8 ± 10.5[77]	−143.3
BBu_3	−283.3 ± 10.9[77]	−274.6
BF_2Me	−832.6 ± 12.6[77]	−809.4
BF_2Et	−875 ± 34[77]	−819.0
BF_2Vi	−715 ± 34[77]	−695.8
$BH(OMe)_2$	−582.4 ± 6.3[99]	−579.8
$BH(O^iPr)_2$	−729.7 ± 3.3[97]	−719.7
$B(OMe)_3$	−902.5 ± 4.1[93]	−898.6
$B(OEt)_3$	−1002.5 ± 5.0[96]	−1000.8
$B(NMe_2)_3$	−275.7 ± 5.0[94]	−239.6
BH_2OH	−292.9 ± 4.2[100]	−274.0
$BH(OH)_2$	−643.5 ± 8.4[100]	−646.3

The compounds considered by Benson and co-workers include methyl, ethyl, and vinyl substituted difuoroboranes with reference values −826.6 ± 12.6, −875 ± 34, and −715 ± 34 kJ mol^{-1}, respectively.[31,77] These data have been derived from ion appearance potentials in electron impact measurements by Steele and co-workers.[98] Owing to the limitations of the method and the assumptions required to be made in the calculation of enthalpies of formation, some very large uncertainties have been assigned to the reported values. A comparison of the data with our W1X-1 enthalpies (−809.4, −819.0, and −695.8 kJ mol^{-1}, respectively) indicates that the authors have been wise in doing so as the reference values for methyl- and ethyldifluoroborane agree with computational predictions only within 3σ confidence intervals. This casts considerable doubt on the validity of these reference values.

The reference values for boronic acid esters dimethyl- and diisopropylboronate,[31] −582.4 ± 6.3[99] and −729.7 ± 3.3 kJ mol^{-1},[97] respectively, and boric acid esters trimethyl- and triethylborate,[31] −902.5 ± 4.1[93] and −1002.5 ± 5.0 kJ mol^{-1},[96] respectively, have been derived from hydrolysis enthalpies. All values are in good agreement with our W1X-1 calculations (−579.8, −719.7, −898.6, and −1000.8 kJ mol^{-1}, respectively), save for diisopropylboronate for which the difference between reference and computational values exceeds their combined 2σ confidence interval, albeit only slightly.

The reference value for tris(dimethylamino)borane given in Table 3, −275.7 ± 5.0 kJ mol^{-1},[31,94] is based on its enthalpy of

hydrolysis in an acidic solution. It differs significantly from the W1X-1 result (−239.6 kJ mol^{-1}) even when considering 3σ confidence intervals. In this case, the ancillary thermochemical data used in the derivation of the quantity appears just and the description of the original experimental work offers no immediate explanation to the discrepancy. Nevertheless, given the proven performance of W1X-1 in predicting the standard enthalpies of formation of boron compounds, we consider the calculated value to be the more accurate of the two.

Benson and co-workers have used the reference values −292.9 ± 4.2 and −643.5 ± 8.4 kJ mol^{-1}, for borinic and boronic acid, respectively.[31,100] These are from the work of Porter and Gupta and were determined by mass spectrometric kinetic analysis of the reaction of diborane with orthoboric acid. The reference value for boronic acid is an excellent match with our calculated W1X-1 result (−646.3 kJ mol^{-1}) but the value for borinic acid differs significantly from the W1X-1 prediction (−274.0 kJ mol^{-1}) even when considering 3σ confidence intervals. However, the ancillary data used to derive the experimental enthalpies are not entirely accurate (for example, 31.4 kJ mol^{-1} was used for the gas phase enthalpy of formation of diborane) and the confidence intervals associated with them are, subsequently, too narrow.

Interestingly, the reference set of Benson and co-workers does not contain triphenylborane, a key species in boron chemistry. Its experimental standard enthalpy of formation, 130.1 ± 8.4 kJ mol^{-1}, is based on enthalpy of hydrolysis.[101] A later investigation on the sublimation enthalpy of triphenylborane[102] gave 155.4 ± 8.4 kJ mol^{-1} for the enthalpy of formation using ancillary data from Pedley and Rylance.[78] These values are statistically different even within 3σ confidence intervals and also *ca.* 150 kJ mol^{-1} less endothermic than our W1X-1 prediction in Table 1 (293.3 kJ mol^{-1}). Given the consistency of our computational results and the large number of ancillary data required to arrive at the experimental values, we strongly argue in favour of our computational prediction. It is plausible that the experimental data of triphenylborane was excluded by Benson and co-workers for its anomalously low value.

Considered as a whole, Table 3 demonstrates a problem common to all group contribution methods: the reliability of reference values used in the derivation of group contributions. Even though the majority of data are accurate within the given confidence intervals, large uncertainties are detrimental to the fitting process and lead to inaccurate group contributions and thereby to poor estimates of thermochemical properties. In some instances, such as with organosilicon compounds,[31] inconsistencies in the reference data have completely prevented the determination of an internally consistent set of group contributions by experimental means. As shown by us[32,33] and by others,[103–107] a simple fix to the problem is offered by theoretical approaches and high-level composite methods in particular. In the following, we pursue this avenue and determine Benson group contributions for boron using the high-level W1X-1 data in Table 1.

Determination of Benson thermochemical group contributions for boron and their application in estimating the gas phase standard enthalpies of formation of boron compounds

Group contributions for 52 Benson groups and group pairs involving boron were derived from the W1X-1 thermochemical data by fitting and the results are presented in Tables 4 and 5 We have adopted the convention of Holmes and Aubry to round the values to the nearest integer to underline the fact that group contribution methods yield only reliable estimates of thermochemical parameters.[8,9] In the case of aryl substituted species, Benson groups such as C_B–$(C_B)_2$(B) always occur in pairs that prevents the easy assignment of unambiguous values for individual groups. Though some authors have chosen to assign arbitrary reference values to some key groups,

Table 4 Thermochemical Benson group contributions for standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}), entropies ($S°$ 298K, J K^{-1} mol^{-1}), and heat capacities (C_p, J K^{-1} mol^{-1}) derived from results of W1X-1 calculations

Group [a]	$\Delta_f H°$ 298K	$S°$ 298K	C_p 298K	C_p 500K	C_p 1000K
B–(C)$(H)_2$	74	134	21	28	41
B–$(C_D)(H)_2$	65	138	16	25	41
B–$(H)_2$(N)	49	120	15	26	42
B–$(H)_2$(O)	94	113	18	28	46
B–$(C)_2$(H)	45	67	17	20	28
B–$(C_D)_2$(H)	26	69	9	16	29
B–(H)$(N)_2$	77	38	13	21	34
B–(H)$(O)_2$	102	27	15	25	35
B–(C)(C_D)(H)	36	71	13	19	30
B–(C)(H)(N)	26	43	12	20	30
B–(C)(H)(O)	66	43	14	22	35
B–$(C)_3$	16	−9	15	16	16
B–$(C)_2(C_D)$	12	−6	11	12	13
B–$(C)_2$(N)	4	−32	9	14	18
B–$(C)_2$(O)	42	−32	11	15	19
B–$(C)(C_D)_2$	8	−1	8	8	12
B–(C)$(F)_2$ [b]	−766	180	31	40	50
B–$(C_D)(F)_2$ [b]	−766	180	31	40	50
B–(C)$(O)_2$	73	−47	13	18	23
B–$(C_D)_3$	2	28	1	−2	3
B–$(C_D)(O)_2$	74	−36	11	15	19
C–(B)(C)$(H)_2$	−11	28	22	33	50
C–(B)$(C_D)(H)_2$	−15	23	19	34	47
C–(B)$(C)_2$(H)	19	−60	22	32	42
C–(B)$(C)_3$	44	−140	21	31	35
C_D–(B)(C_D)(H)	44	12	19	30	40
N–(B)$(H)_2$	−131	114	24	33	46
N–(B)(C)(H)	−79	32	18	23	33
N–(B)$(C)_2$	−34	−57	15	19	24
O–(B)(H)	−373	116	16	23	30
O–(B)(C)	−296	34	10	11	15
S–(B)(C)	−63	52	20	21	19
B–$(H)_2(H_{BR})_2$ [c]	20	122	24	39	63
B–(C)(H)$(H_{BR})_2$ [c]	6	42	22	34	51
B–$(C)_2(H_{BR})_2$ [c]	−11	−39	20	28	39
cis-Corr., B_2H_6	3	−1	−1	−1	0
Ring strain, BO_2C_2	−12	109	−19	−20	−6

[a] Values of groups B–$(O)_3$≡B–$(S)_3$≡B–$(N)_3$ are set to match those of N–$(C)_3$ by Domalski and Hearing.[74,75] [b] Values set to be identical to avoid linear dependencies. [c] H_{BR} = bridging hydrogen.

Table 5 Thermochemical Benson group pair contributions for standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}), entropies ($S°$ 298K, J K^{-1} mol^{-1}), and heat capacities (C_p, J K^{-1} mol^{-1}) derived from results of W1X-1 calculations

Group pair	$\Delta_f H°$ 298K	$S°$ 298K	C_p 298K	C_p 500K	C_p 1000K
B–(C$_B$)(H)$_2$ + C$_B$–(C$_B$)$_2$(B)	92	84	31	49	70
B–(C$_B$)$_2$(H) + 2 × C$_B$–(C$_B$)$_2$(B)	92	−41	40	64	83
B–(C)(C$_B$)(H) + C$_B$–(C$_B$)$_2$(B)	65	11	28	43	55
B–(C$_B$)(C$_D$)(H) + C$_B$–(C$_B$)$_2$(B)	55	14	23	38	55
B–(C$_B$)(H)(O) + C$_B$–(C$_B$)$_2$(B)	90	−5	29	46	63
B–(C)$_2$(C$_B$) + C$_B$–(C$_B$)$_2$(B)	42	−52	25	34	40
B–(C)(C$_B$)$_2$ + 2 × C$_B$–(C$_B$)$_2$(B)	67	−120	39	59	72
B–(C)(C$_B$)(C$_D$) + C$_B$–(C$_B$)$_2$(B)	36	−55	25	32	37
B–(C)(C$_B$)(O) + C$_B$–(C$_B$)$_2$(B)	68	−79	26	36	44
B–(C$_B$)$_3$ + 3 × C$_B$–(C$_B$)$_2$(B)	86	−175	52	80	103
B–(C$_B$)$_2$(C$_D$) + 2 × C$_B$–(C$_B$)$_2$(B)	60	−118	37	57	74
B–(C$_B$)(C$_D$)$_2$ + C$_B$–(C$_B$)$_2$(B)	32	−58	23	33	41
B–(C$_B$)(O)$_2$ + C$_B$–(C$_B$)$_2$(B)	106	−85	26	39	47
O–(B)(C$_B$) + C$_B$–(C$_B$)$_2$(O)	−279	43	11	11	13

we have opted to use group pair values. This is well-justified as the individual contributions have no physical meaning.

Before discussing the application potential of the data in Tables 4 and 5 in more detail, we point out that the W1X-1 enthalpies given in Table 1 already illustrate that the underlying approximation of additivity of thermochemical properties holds well for organoboron compounds considered herein. For example, the calculated standard enthalpies of formation for the methylborane series BH_3, BH_2Me, $BHMe_2$, and BMe_3 (103.9, 32.3, −39.7, and −109.6 kJ mol^{-1}, respectively) show that each consecutive H-to-Me replacement on boron alters the standard enthalpy of formation by a constant factor of *ca.* −71 kJ mol^{-1}. The same is true for the corresponding ethyl series, in which case every H-to-Et replacement affects the enthalpy by *ca.* −82 kJ mol^{-1}. Similarly, a comparison between the methyl- and ethylborane series allows to determine the effect of Me-to-Et substitution on boron and this value turns out to be *ca.* −11 kJ mol^{-1}. The same correction applies equally well to any similar Me-to-Et replacement within compounds given in Table 1 as shown, for example, by the calculated standard enthalpies of formation for methyl- and ethyldifluoroborane (−809.4 and −819.0 kJ mol^{-1}, respectively) with a difference of *ca.* 10 kJ mol^{-1}. In contrast, if the Me-to-Et correction is calculated using Skinner's reference values,[77] two vastly different numbers are obtained: *ca.* −10 kJ mol^{-1} from data for trimethyl- and triethylborane (−122.4 ± 23.0 and −152.8 ± 10.5 kJ mol^{-1}, respectively) or −48 kJ mol^{-1} from methyl- and ethyldifluoroborane (−826.6 ± 12.6 and −875 ± 34 kJ mol^{-1}, respectively), which completely masks the validity of the additivity approximation.

Even though the individual Benson group contributions carry no physical meaning, it is instructive to compare the values in Table 4 to those originally reported by Benson and co-workers.[31] The assessment of ten group contributions common to both studies shows that the agreement varies from excellent (C–(B)(C)(H)$_2$, difference of 2 kJ mol^{-1}) to very poor (O–(B)(H), difference of 110 kJ mol^{-1}). This is affected in part by minor variations in the reference values used in the two works (for example, B–(O)$_3$≡B–(S)$_3$≡B–(N)$_3$, 116.5[74,75] *vs.* 102.1 kJ mol^{-1})[31] but even more so by the accuracy of the employed reference data as discussed above. In our case, the fitted group contributions fully reproduce the reference W1X-1 thermochemical data used to derive them in the case of enthalpies (MAD 1.6 kJ mol^{-1}, maximum deviation 11.0 kJ mol^{-1}) and heat capacities (MAD 0.8 J K^{-1} mol^{-1}, maximum deviation 3.9 J K^{-1} mol^{-1}), while a slightly poorer fit is found in the case of entropies (MAD 3.2 J K^{-1} mol^{-1}, maximum deviation −19.1 J K^{-1} mol^{-1}). Thus, the data in Tables 4 and 5 are fully self-consistent and allow for quick and reliable on-the-fly estimation of thermodynamic properties of a wide range of boron compounds within the limits of the employed parametrization.

To illustrate the usefulness of group contributions given in Tables 4 and 5, we used them to estimate the standard enthalpies of formation of 13 boron compounds for which experimental reference values have been reported by Skinner[77,93] and others (Table 6).[89] Even though the smallest of the systems in question could easily be subjected to W1X-1 treatment, molecules such as triheptyl- and trioctylborane have more than 20 non-hydrogen atoms, making high-level calculations prohibitively expensive in terms of both time and com-

Table 6 Reference (Ref.) and estimated (Benson) gas phase standard enthalpies of formation ($\Delta_f H°$ 298K, kJ mol^{-1}) of selected boron compounds

Molecule	Ref.	Benson
B^{i}Bu$_3$	−279.9 ± 5.4[77]	−274
B^{s}Bu$_3$	−245.6 ± 25.1[77]	−242
BHex$_3$	−396.6 ± 10.9[77]	−391
BHept$_3$	−457.7 ± 8.4[77]	−453
BOct$_3$	−520.9 ± 8.4[77]	−515
BF$_2$^{i}Pr	−887 ± 34[77]	−832
BBu$_2$(OH)	−546.4 ± 16.7[77]	−520
B(OPr)$_3$	−1091.6 ± 10.0[93]	−1059
B(OBu)$_3$	−1169.0 ± 10.5[93]	−1121
B(SEt)$_3$	−285.3 ± 2.9[89]	−269
B(SPr)$_3$	−334.7 ± 3.3[89]	−331
B(SBu)$_3$	−394.1 ± 4.2[89]	−393
B(SPe)$_3$	−463.2 ± 5.4[89]	−454

putational resources. In these cases, the use of group contribution method allows for a quick screening of the reference values for obvious outliers that could easily arise from the use of estimated thermochemical quantities.

As shown by the data in Table 6, standard enthalpies of formation calculated from Benson group contributions are in good agreement with the reference values in the majority of cases, thereby building confidence that the estimations made in deriving the reference values have been justified. The most obvious outlier is isopropyl difluoroborane, whose reference value, −887 ± 34 kJ mol^{-1},[77] is associated with a very large uncertainty. Based on the earlier discussion pertaining to methyl- and ethyldifluoroborane, we conclude that the reference value for isopropyl difluoroborane continues the series and is most likely erroneous.

The estimated standard enthalpies of formation of heavier trialkylthioborates[89] are in good agreement with the reference values, excluding data for triethylthioborate. In the preceding analyses, we noted that the experimental value for trimethylthioborate,[89] though given with a narrow 2σ confidence interval, should be adjusted by *ca.* 40 kJ mol^{-1} to −199.1 kJ mol^{-1}. We can now use the high-level W1X-1 computational data for it along with a correction term for Me-to-Et substitution on sulphur, −23 kJ mol^{-1}, calculated from experimental enthalpies of formation for dialkylsulfides,[3] as another means to estimate the standard enthalpy of formation of triethylthioborate. Adding three correction terms to the W1X-1 enthalpy of trimethylthioborate gives −268 kJ mol^{-1} as the standard enthalpy of formation of triethylthioborate, in excellent agreement with the estimate based on group contribution values alone. The data for tripropyl- and tributylborate in Table 6 can also be subjected to similar analysis, resulting in standard enthalpies of formation of −1063 and −1126 kJ mol^{-1}, respectively, based on the experimental values for triethylborate[96] and relevant dialkylethers.[3] In further support of our enthalpy estimates in Table 6, we used the W1X-1 method to calculate the standard enthalpy of formation of triethylthioborate, the smallest of the three problematic systems discussed herein. The result, −270.0 kJ mol^{-1}, is another testament of the effectiveness of the group contribution method and the ability of the data in Tables 4 and 5 to yield reliable estimates of thermochemical properties.

As a final exercise demonstrating the usefulness of group contribution values in Tables 4 and 5, we used them to calculate the standard enthalpies of formation for a series of monosubstituted phenylboronic acids. These are an interesting class of compounds with diverse applications in synthesis and biological, medicinal, and materials chemistry.[108] Furthermore, substituted boronic acids are one of the few groups of organoboron compounds whose thermochemical properties have been investigated by computational means using Gaussian-*n* composite methods, the other being boroxines.[109–111] Specifically, Rao *et al.* have calculated the standard enthalpies of formation of selected monosubstituted phenylboronic acids and their different isomers at the G3 level of theory (Table 7).[109] As the parent compound is included amongst those in Table 1, we have now estimated the enthalpies of all systems investigated by Rao *et al.* with the help of group contributions derived herein. The expected uncertainties of the two different approaches are similar, making a comparison between them particularly illustrative.

The results in Table 7 are an excellent demonstration of the value of group contribution methods in thermochemical analyses. Standard enthalpies of formation calculated using Benson's method fully reproduce the G3 data (MAD of 3 kJ mol^{-1}) in all but a single case. This is because the *ortho*-isomer of fluorophenylboronic acid contains an intramolecular O–H···F hydrogen bond, whose enthalpic content has not been parametrized within the used group contributions. A value for it can, however, be obtained using an average of calculated data for related intramolecular hydro-

Table 7 Comparison between calculated (G3) and estimated (Benson) standard gas phase enthalpies of formation ($\Delta_f H°$, 298 K, kJ mol^{-1}) of monosubstituted phenylboronic acids

Molecule	Benson groups[a]	G3[109]	Benson	Diff.
$C_6H_5B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 5 × C_B–$(C_B)_2$(H)	−570.7	−571	0
p-$C_6H_4(CH_3)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(C), C–$(C_B)(H)_3$	−605.3	−603	2
m-$C_6H_4(CH_3)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(C), C–$(C_B)(H)_3$	−604.2	−603	1
o-$C_6H_4(CH_3)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(C), C–$(C_B)(H)_3$, *o*-corr.[b]	−597.0	−601	−4
p-$C_6H_4(NH_2)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(N), N–$(C_B)(H)_2$	−570.9	−567	4
m-$C_6H_4(NH_2)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(N), N–$(C_B)(H)_2$	−565.1	−567	−2
o-$C_6H_4(NH_2)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(N), N–$(C_B)(H)_2$, *o*-corr.[b]	−575.2	−571	4
p-$C_6H_4(OH)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), O–(C_B)(H), C_B–$(C_B)_2$(O)	−751.5	−750	2
m-$C_6H_4(OH)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), O–(C_B)(H), C_B–$(C_B)_2$(O)	−746.1	−750	−4
o-$C_6H_4(OH)B(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), O–(C_B)(H), C_B–$(C_B)_2$(O), *o*-corr.[b]	−765.8	−770	−4
p-$C_6H_4FB(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(F)	−771.7	−766	6
m-$C_6H_4FB(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(F)	−770.0	−766	4
o-$C_6H_4FB(OH)_2$	C_B–$(C_B)_2$(B) + B$(C_B)$$(O)_2$, 2 × O–(B)(H), 4 × C_B–$(C_B)_2$(H), C_B–$(C_B)_2$(F), *o*-corr.[b]	−784.0	−769	15

[a] Literature values (kJ mol^{-1}) for Benson groups of carbon and oxygen taken from Domalski and Hearing:[74,75] C_B–$(C_B)_2$(H) = 13.81, C_B–$(C_B)_2$(C) = 23.64, C–$(C_B)(H)_3$ = −42.26, C_B–$(C_B)_2$(N) = −1.30, N–$(C_B)(H)_2$ = 19.25, C_B–$(C_B)_2$(O) = −4.75, O–(C_B)(H) = −160.30, C_B–$(C_B)_2$(F) = −181.26. [b] *ortho*-Corrections (kJ mol^{-1}): B$(OH)_2$–CH_3≡NO_2–CH_3 = 2.00, B$(OH)_2$–NH_2≡NO_2–NH_2 = −4.00, B$(OH)_2$–OH≡COOH–OH = −20.00, B$(OH)_2$–F≡CH_3–F = −3.30.

gen bonds,[112] *ca.* −10 kJ mol^{-1}, yielding −779 kJ mol^{-1} for the estimated enthalpy, fully on par with the result from G3 level calculation (−784 kJ mol^{-1}). In contrast to the many hours of CPU time required to obtain the G3 data in Table 7, the estimates based on Benson group contributions were determined within a click of a single button. While this may seem like an insignificant saving of time and resources in the current case, it becomes less so when the number of thermochemical parameters to be estimated is counted in hundreds and/or if the size of the systems in question increases considerably.

Conclusions

It this contribution, we investigated 116 boron compounds with high-level composite quantum chemical methods to determine their thermochemical properties. The results were compared to FPD benchmark values as well as extant experimental data and reference values based on different estimations. The calculated thermochemical properties were used to derive Benson group contributions for standard gas phase enthalpy of formation, entropy, and heat capacity for 52 Benson groups and group pairs involving boron that can, in turn, be employed in estimating thermochemical propertied of compounds that have not been subjected to experimental studies and/or cannot be treated with high-level theoretical methods.

The most important results of this work can be summarized as follows:

High-level W1X-1 results are in excellent agreement with FPD benchmark values and indicate that the experimental gas phase standard enthalpies of formation of key boron compounds are, for the most part, accurate within the reported uncertainties. However, the 2σ confidence intervals of experimental values are often substantially larger than those of computational predictions, which can lead to considerable error, for example, if more than one of them are required to calculate an unknown quantity. In this respect, computational results suggest that the experimental standard enthalpy of formation of orthoboric acid, a key species to which many other reported enthalpies are related, is slightly too endothermic. High-level calculations also show that the standard enthalpies of formation reported for trimethylthioborate and triphenylborane are erroneous and should be replaced with the significantly more accurate W1X-1 predictions.

Many of the experimental thermochemical results reported for boron compounds are based on estimated or by other means approximated quantities. Computational analysis of a selected set of compounds from this category revealed that the very large uncertainties assigned to the reported values are well justified. In many cases, the given 2σ confidence intervals are still too conservative as significant differences are observed between reference values and high-level computational data. Nevertheless, the reported enthalpies are in many cases sufficiently accurate to be used as such in various applications. However, the combined use of these values, such as in a training set for the development of group additivity approaches, is beyond their applicability, and high-level computational data should be used instead to achieve sufficient accuracy.

Computationally derived Benson group contributions show that the approximation of additivity of thermochemical properties holds well also for boron compounds. This allows, for example, the accurate estimation of standard enthalpies of formation of many organoboron species irrespective of their size and complexity, provided that the necessary group contributions have been determined. Application of this approach to a diverse set of boron compounds demonstrated that the experimental reference values for several difluoroboranes, trialkylborates, and trialkylthioborates are noticeable outliers and, therefore, most likely in error. This conclusion was further supported by bond enthalpy considerations and accurate W1X-1 level results. In another example, the standard enthalpies of formation of monosubstituted phenylboronic acids were estimated with the group additivity method and the results fully reproduce the G3 level data with a fraction of the computational cost.

Even though group additivity methods might seem archaic in the era of high-performance computing, they offer a very powerful approach whenever thermochemical data are required for bigger molecular systems or for a large group of compounds. In these cases, high-level quantum chemical calculations become prohibitively expensive or even impossible. The results reported herein can be implemented in any thermochemical software utilizing Benson's approach, allowing their extension to boron compounds and, therefore, to new application areas. We note that even though machine learning models are becoming the state-of-the-art in numerous applications, the prediction of thermochemical properties making no exception, their adaptation beyond elements C, H, N, and O and wide-scale implementation will take time. In this respect, the high-level W1X-1 enthalpies reported herein can also be used to train the algorithms in machine learning models due to their significantly better accuracy over existing experimental data.

Author contributions

H. T. V.: conceptualization, investigation, formal analysis, writing – original draft preparation. J. M. R.: validation, supervision, writing – review & editing. E. T. K.: conceptualization, writing – original draft preparation. H. M. T.: resources, writing – review & editing, supervision, project administration, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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IV

ADDITION/CORRECTION TO "HIGH-LEVEL AB INITIO PREDICTIONS OF THERMOCHEMICAL PROPERTIES OF ORGANOSILICON SPECIES: CRITICAL EVALUATION OF EXPERIMENTAL DATA AND A RELIABLE BENCHMARK DATABASE FOR EXTENDING GROUP ADDITIVITY APPROACHES"

by

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Addition/Correction

Addition/Correction to "High-Level Ab Initio Predictions of Thermochemical Properties of Organosilicon Species: Critical Evaluation of Experimental Data and a Reliable Benchmark Database for Extending Group Additivity Approaches"

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Recently, we reported thermochemical properties of a number of organosilicon species calculated at the W1X-1 level of theory.[1] We have since come to the realization that the atomic reference values used in our original work (Table S1, ESI) were inadvertently based on unrestricted MP2 energies even though the composite W1X-1 protocol uses restricted open-shell wave functions throughout.[2,3] In this Addition/Correction, we report the revised thermochemical data and demonstrate that they do not change the conclusions of the original paper. The results do, however, provide a cautionary note on the calculation of high-level thermochemical properties for molecules with many heavy (non-hydrogen) atoms.

The performance of restricted open-shell, unrestricted, unrestricted spin contamination corrected, and unrestricted Brueckner doubles variants of the original W1 theory have been discussed in detail by Petersson and co-workers.[4] The four slightly different methods were found to be virtually indistinguishable on the basis of the data calculated for the G2/97 test set. Though this is certainly true and holds in general for small molecules, even sub-kJ mol^{-1} level systematic variations in atomic reference energies can lead to large differences when the size of the system in question increases considerably. This is clearly shown by our work even though only one of the components of the W1X-1 methodology was based on an unrestricted reference determinant.

Table 1 includes the W1X-1(UMP2) and CBS-QB3 gas phase standard enthalpies of formation published in our original contribution along with the revised W1X-1(ROMP2) values. A comparison of the two W1X-1 data sets shows that the different atomic reference values lead to enthalpies based on restricted open-shell MP2 wave functions being systematically more exothermic (mean absolute difference of 4.2 kJ mol^{-1}) compared to the values calculated with the unrestricted formalism. The difference is naturally the smallest for systems with the least number of heavy atoms (e.g., SiH_4, 0.8 kJ mol^{-1}) and grows with respect to the molecular size (e.g., $SiPh_2(OMe)_2$, 8.5 kJ mol^{-1}). As a consequence, the revised W1X-1(ROMP2) enthalpies are now in excellent harmony with the CBS-QB3 values for monosilanes **I**, with a positive mean signed deviation (MSD) of only 3 kJ mol^{-1}. However, the opposite is true for all other compound classes **II**−**V**, **VI**−**IX**, **X**−**XII**, and **XIII** and **XIV**, and the associated MSD values, −5, −8, −17, and −21 kJ mol^{-1}, respectively, are now significantly more negative than those based on the prior W1X-1(UMP2) data.

Table 2 lists well-established experimental gas phase standard enthalpies of formation for 13 reference silicon compounds used in our original paper along with the calculated values. Unsurprisingly, the W1X-1(UMP2) and W1X-1(ROMP2) values are nearly identical for the structurally simplest alkylsilanes and silanols, with larger differences observed for systems with multiple methyl and ethyl substituents, such as Si_2Me_6 and $Si(OEt)_4$, in which case the W1X-1(ROMP2) and W2 data are in good agreement with each other. The conclusions in our original paper are unaffected by the changes in the calculated values, and we continue to stress the importance of obtaining accurate experimental thermochemical data on compounds such as $SiMe_4$ and $Si(OEt)_4$ for which large differences between reference values and W2 level calculations are observed.

In our original paper, we noted significant differences between our W1X-1(UMP2) values for the methylsilane series and the G4 enthalpies reported by Janbazi et al.,[7,8] +26.2, −87.3, −160.0, and −233.6 kJ mol^{-1}, for SiH_3Me, SiH_2Me_2, $SiHMe_3$, and $SiMe_4$, respectively. These differences persist even after our data have been adjusted to use atomic energies based on restricted open-shell MP2 wave functions (see Table 2). Considering the identical values given by W1X-1(ROMP2) and W2 for the standard enthalpy of formation of $SiMe_4$, −212.4 and −212.8 kJ mol^{-1}, respectively, the G4 prediction by Janbazi et al. remains questionable even though it matches the well-established experimental value, −233.2 ± 3.2 kJ mol^{-1}.

The last effort reported in our original contribution focused on using the calculated W1X-1 thermochemical data to derive Benson group contributions for 60 silicon-based groups and group pairs. The revised group values based on the W1X-1(ROMP2) energies are given in Tables 3 and 4. We note that the values in Table 3 are nearly, within a few kJ mol^{-1}, identical with the original data. In line with the discussion in the original paper, these values can be considered superior over those reported by Janbazi et al. and Becerra and Walsh. The values for group pairs given in Table 4

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Table 1. Calculated Gas Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}) of Monosilanes 1−42, Polysilanes 43−49, Silanols and Alkoxysilanes 50−80, Acyclic Siloxanes 81−150, Cyclic Siloxanes 151−158, and Silylamine 159[a]

			$\Delta_f H^\circ_{298K}$		
group	molecule	chemical formula	CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)
I	1	SiH_4	27.0	35.9	36.7
	2	SiH_3Me	−27.6	−23.8	−22.5
	3	SiH_3Et	−34.4	−32.8	−31.1
	4	SiH_3Vi	94.3	96.9	98.6
	5	SiH_3Ph	130.6	124.8	131.0
	6	$SiH_3{}^iPr$	−52.7	−52.7	−50.5
	7	$SiH_3{}^sBu$	−70.2	−72.3	−69.6
	8	SiH_3(3-Pe)	−86.8	−90.6	−87.4
	9	SiH_2Me_2	−85.1	−85.9	−84.1
	10	SiH_2EtMe	−91.9	−94.8	−92.6
	11	SiH_2MeVi	35.9	34.0	36.2
	12	SiH_2MePh	70.5	63.3	67.4
	13	$SiH_2Me{}^iPr$	−110.7	−114.9	−112.2
	14	$SiH_2Me{}^sBu$	−128.0	−134.2	−131.0
	15	SiH_2Me(3-Pe)	−143.8	−151.7	−148.0
	16	SiH_2Et_2	−98.8	−103.7	−101.0
	17	SiH_2EtPh	62.9	52.7	58.3
	18	SiH_2Vi_2	156.6	153.5	156.2
	19	SiH_2Ph_2	223.4	210.3	216.8
	20	$SiHMe_3$	−145.2	−149.9	−147.7
	21	$SiHEtMe_2$	−152.1	−158.7	−156.0
	22	$SiHMe_2Vi$	−24.8	−30.6	−28.0
	23	$SiHMe_2Ph$	8.5	−2.2	2.4
	24	$SiHMe_2{}^iPr$	−171.0	−178.7	−175.6
	25	$SiHMe_2{}^sBu$	−188.4	−197.9	−194.3
	26	$SiHMe_2$(3-Pe)	−204.3	−215.3	−211.2
	27	$SiHEtMePh$	−0.8	−12.7	−7.7
	28	$SiHMeVi_2$	95.1	88.2	91.4
	29	$SiHMePhVi$	127.2	115.7	120.8
	30	$SiHVi_3$	215.4	207.8	211.5
	31	$SiHPhVi_2$	247.5	234.9	240.4
	32	$SiMe_4$	−207.4	−215.0	−212.4
	33	$SiEtMe_3$	−214.4	−223.7	−220.6
	34	$SiMe_3Vi$	−87.6	−96.5	−93.3
	35	$SiMe_3Ph$	−55.2	−68.4	−63.4
	36	$SiMe_2Vi_2$	31.8	21.9	25.5
	37	$SiEtMe_2Ph$	−64.9	−78.8	−73.3
	38	$SiMe_2PhVi$	63.2	49.1	54.6
	39	$SiMe_2Ph_2$	94.0	76.0	83.4
	40	$SiMeVi_3$	150.1	139.9	143.9
	41	$SiMePhVi_2$	180.4	166.1	172.1
	42	$SiEt_4$	−238.8	−251.9	−247.4
II	43	Si_2H_6	74.2	81.1	82.7
	44	Si_2H_5Me	20.1	22.9	24.9
	45	$Si_2H_4Me_2$	−33.4	−34.6	−32.1
	46	Si_2Me_6	−267.3	−280.3	−275.9
III	47	Si_3H_8	113.7	120.4	122.7
IV	48	Si_4H_{10}	151.7	158.4	161.5
V	49	Si_5H_{12}	189.4	196.1	200.0
VI	50	SiH_3OH	−286.7	−280.1	−278.7
	51	SiH_2MeOH	−352.4	−350.7	−348.9
	52	SiH_2EtOH	−359.3	−359.3	−357.0
	53	$SiHMe_2OH$	−417.7	−419.7	−417.4
	54	$SiMe_3OH$	−483.4	−488.2	−485.4
	55	SiH_3OMe	−253.7	−245.8	−243.9
	56	$SiH_2Me(OMe)$	−319.7	−316.4	−314.1
	57	$SiHMe_2(OMe)$	−384.9	−385.0	−382.3
VII	58	$SiH_2(OH)_2$	−633.2	−628.7	−626.8

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Table 1. continued

group	molecule	chemical formula	$\Delta_f H^\circ_{298K}$ CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)
	59	$SiH_2(OMe)_2$	−565.7	−557.7	−554.9
	60	$SiHMe(OMe)_2$	−635.1	−630.3	−627.0
	61	$SiHVi(OMe)_2$	−513.6	−509.5	−505.7
	62	$SiHPh(OMe)_2$	−482.7	−483.3	−477.6
	63	$SiMe_2(OMe)_2$	−705.1	−702.3	−698.5
	64	$SiMeVi(OMe)_2$	−584.6	−582.4	−578.1
	65	$SiMePh(OMe)_2$	−555.0	−556.8	−550.6
	66	$SiVi_2(OMe)_2$	−464.3	−462.6	−457.9
	67	$SiPhVi(OMe)_2$	−435.4	−437.4	−430.7
	68	$SiPh_2(OMe)_2$	−406.9	−412.4	−403.9
VIII	**69**	$SiH(OH)_3$	−988.7	−985.9	−983.5
	70	$SiMe(OMe)_2OH$	−992.3	−986.6	−982.7
	71	$SiEt(OMe)_2OH$	−999.1	−994.3	−990.0
	72	$SiMe(OMe)_3$	−957.0	−948.6	−944.3
	73	$SiEt(OMe)_3$	−964.3	−956.7	−951.9
IX	**74**	$Si(OH)_4$	−1344.2	−1341.7	−1338.7
	75	$Si(OMe)_3OH$	−1243.4	−1232.3	−1227.8
	76	$Si(OEt)(OMe)_2OH$	−1277.0	−1267.5	−1262.6
	77	$Si(OEt)_2(OMe)OH$	−1310.8	−1302.8	−1297.4
	78	$Si(OMe)_4$	−1209.9	−1195.8	−1190.9
	79	$Si(OEt)(OMe)_3$	−1243.8	−1231.3	−1225.9
	80	$Si(OEt)_4$	−1345.7	−1337.7	−1330.9
X	**81**	$O(SiH_3)_2$	−356.3	−339.7	−337.6
	82	$O(SiMe_3)(SiH_3)$	−556.8	−550.7	−547.1
	83	$O(SiF_3)(SiH_3)$	−1620.9	−1605.9	−1602.9
	84	$O(SiH_2Me)(SiH_3)$	−422.3	−410.7	−408.1
	85	$O(SiH_2Vi)(SiH_3)$	−300.1	−289.3	−286.2
	86	$O(SiH_2Ph)(SiH_3)$	−265.8	−259.6	−254.7
	87	$O(SiH_2F)(SiH_3)$	−774.9	−759.8	−757.3
	88	$O(SiHMe_2)(SiH_3)$	−489.3	−481.0	−477.9
	89	$O(SiHVi_2)(SiH_3)$	−248.0	−241.3	−237.3
	90	$O(SiHF_2)(SiH_3)$	−1204.1	−1190.3	−1187.6
	91	$O(SiHMePh)(SiH_3)$	−335.7	−332.7	−327.3
	92	$O(SiH_2Me)_2$	−488.3	−481.4	−478.3
	93	$O(SiHMe_2)(SiH_2Me)$	−555.1	−550.7	−548.0
	94	$O(SiH_2Ph)(SiH_2Me)$	−330.6	−329.9	−324.5
	95	$O(SiMe_3)(SiH_2Me)$	−622.5	−621.2	−617.2
	96	$O(SiHMe_2)_2$	−621.7	−621.6	−617.6
	97	$O(SiMe_3)(SiHMe_2)$	−689.1	−690.8	−686.3
	98	$O(SiMe_3)_2$	−756.2	−760.0	−755.0
	99	$O(SiH_2Vi)_2$	−244.5	−238.9	−234.9
	100	$O(SiH_2F)_2$	−1192.1	−1179.1	−1176.4
	101	$O(SiHF_2)(SiH_2F)$	−1619.7	−1607.7	−1604.6
	102	$O(SiF_3)(SiH_2F)$	−2035.4	−2022.4	−2019.0
	103	$O(SiHF_2)_2$	−2045.5	−2034.6	−2031.3
	104	$O(SiF_3)(SiHF_2)$	−2460.7	−2448.8	−2445.2
	105	$O(SiF_3)_2$	−2874.1	−2861.4	−2857.4
XI	**106**	$SiH_2(OSiH_3)_2$	−771.7	−746.1	−742.7
	107	$SiH_2(OSiH_2Me)(OSiH_3)$	−838.0	−816.3	−812.4
	108	$SiH_2(OSiH_2Vi)(OSiH_3)$	−716.0	−695.9	−691.5
	109	$SiH_2(OSiH_2Ph)(OSiH_3)$	−680.3	−665.7	−659.4
	110	$SiH_2(OSiH_2F)(OSiH_3)$	−1190.8	−1166.0	−1162.2
	111	$SiH_2(OSiMe_3)(OSiH_3)$	−973.7	−958.5	−953.6
	112	$SiH_2(OSiHMe_2)(OSiH_3)$	−905.8	−888.5	−884.1
	113	$SiH_2(OSiHF_2)(OSiH_3)$	−1620.1	−1596.1	−1592.0
	114	$SiH_2(OSiF_3)(OSiH_3)$	−2036.7	−2011.9	−2007.5
	115	$SiH_2(OSiH_2Me)_2$	−904.2	−888.2	−883.8
	116	$SiH_2(OSiHMe_2)(OSiH_2Me)$	−972.0	−959.5	−954.7
	117	$SiH_2(OSiMe_3)(OSiH_2Me)$	−1039.9	−1029.4	−1024.0

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Table 1. continued

group	molecule	chemical formula	$\Delta_f H^\circ_{298K}$ CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)
	118	$SiH_2(OSiH_2F)_2$	−1607.1	−1585.0	−1581.0
	119	$SiH_2(OSiHMe_2)_2$	−1039.4	−1030.3	−1025.0
	120	$SiH_2(OSiMe_3)(OSiHMe_2)$	−1107.2	−1100.2	−1094.3
	121	$SiH_2(OSiMe_3)_2$	−1175.1	−1169.9	−1163.6
	122	$SiHMe(OSiH_3)_2$	−843.2	−821.1	−817.2
	123	$SiHVi(OSiH_3)_2$	−720.8	−699.2	−694.8
	124	$SiHPh(OSiH_3)_2$	−689.0	−671.9	−665.6
	125	$SiHF(OSiH_3)_2$	−1203.6	−1178.3	−1174.5
	126	$SiHMe(OSiH_2Me)(OSiH_3)$	−909.5	−892.1	−887.7
	127	$SiHMe(OSiHMe_2)(OSiH_3)$	−977.0	−963.4	−958.5
	128	$SiHMe(OSiMe_3)(OSiH_3)$	−1045.1	−1033.0	−1027.7
	129	$SiHMe(OSiH_2Me)_2$	−975.5	−962.9	−958.0
	130	$SiHMe(OSiHMe_2)(OSiH_2Me)$	−1043.4	−1034.4	−1029.0
	131	$SiHMe(OSiMe_3)(OSiH_2Me)$	−1111.3	−1104.1	−1098.2
	132	$SiHMe(OSiHMe_2)_2$	−1110.6	−1104.4	−1098.6
	133	$SiHMe(OSiMe_3)(OSiHMe_2)$	−1179.1	−1174.7	−1168.4
	134	$SiHMe(OSiMe_3)_2$	−1246.5	−1243.8	−1237.0
	135	$SiHF(OSiH_2F)(OSiH_3)$	−1622.9	−1594.8	−1594.4
	136	$SiHF(OSiHF_2)(OSiH_3)$	−2051.1	−2027.1	−2022.7
	137	$SiMe_2(OSiH_3)_2$	−915.5	−894.7	−890.3
	138	$SiMe_2(OSiH_2Me)(OSiH_3)$	−981.5	−965.5	−960.6
	139	$SiMe_2(OSiHMe_2)(OSiH_3)$	−1049.1	−1036.6	−1031.2
	140	$SiMe_2(OSiMe_3)(OSiH_3)$	−1116.9	−1106.2	−1100.4
	141	$SiMe_2(OSiH_2Me)_2$	−1047.4	−1036.0	−1030.6
	142	$SiMe_2(OSiHMe_2)(OSiH_2Me)$	−1115.0	−1107.2	−1101.4
	143	$SiMe_2(OSiMe_3)(OSiH_2Me)$	−1182.8	−1176.7	−1170.4
	144	$SiMe_2(OSiMe_3)_2$	−1317.9	−1316.6	−1309.3
	145	$SiMe_2(OSiHMe_2)_2$	−1182.3	−1177.1	−1170.9
	146	$SiMe_2(OSiMe_3)(OSiHMe_2)$	−1250.4	−1246.9	−1240.1
	147	$SiF_2(OSiH_3)_2$	−1625.4	−1598.9	−1594.8
	148	$SiF_2(OSiH_2F)(OSiH_3)$	−2043.8	−2017.1	−2012.7
	149	$SiF_2(OSiH_2F)_2$	−2460.5	−2434.9	−2430.3
XII	**150**	$O(SiH_2OSiH_3)_2$	−1186.1	−1151.9	−1147.1
XIII	**151**	$(OSiH_2)_3$	−1215.7	−1196.3	−1192.4
	152	$(OSiHMe)(OSiH_2)_2$	−1290.0	−1273.4	−1269.0
	153	$(OSiMe_2)(OSiH_2)_2$	−1362.9	−1348.1	−1343.2
	154	$(OSiHMe)_2(OSiH_2)$	−1363.8	−1350.2	−1345.3
	155	$(OSiMe_2)(OSiHMe)(OSiH_2)$	−1436.6	−1424.6	−1419.1
	156	$(OSiHMe)_3$	−1437.3	−1426.6	−1421.2
	157	$(OSiMe_2)_3$	−1653.8	−1648.3	−1641.5
XIV	**158**	$(OSiH_2)_4$	−1656.2	−1623.5	−1618.1
XV	**159**	$NH(SiMe_3)_2$	−454.0	−472.0	−457.5

[a]Used abbreviations: Me = methyl, Et = ethyl, ^{i}Pr = isopropyl, ^{s}Bu = *sec*-butyl, 3-Pe = 3-pentyl, Vi = vinyl, and Ph = phenyl.

Table 2. Experimental (exptl) and Calculated (CBS-QB3, W1X-1(UMP2), W1X-1(ROMP2), and W2) Gas Phase Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}) of 13 Reference Silicon Compounds[a]

molecule	$\Delta_f H^\circ_{298K}$ exptl	CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)	W2
SiH_4	34.3 ± 1.2	27.0	35.9	36.7	
Si_2H_6	79.9 ± 1.5	74.2	81.1	82.7	
Si_3H_8	120.9 ± 4.4	113.7	120.4	122.7	
SiH_3Me	−29.1 ± 4.0	−27.6	−23.8	−22.5	
SiH_2Me_2	−94.7 ± 4.0	−85.1	−85.9	−84.1	
$SiHMe_3$	−163.4 ± 4.0	−145.2	−149.9	−147.7	
$SiMe_4$	−233.2 ± 3.2	−207.4	−215.0	−212.4	−212.8
Si_2Me_6	−303.7 ± 5.5	−267.3	−280.3	−275.9	−277.0
$Si(OH)_4$	−1351.3 ± 1.7	−1344.2	−1341.7	−1338.7	
$SiMe_3(OH)$	−500.0 ± 3.0	−483.4	−488.2	−485.4	

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Table 2. continued

molecule	$\Delta_f H^\circ_{298K}$				
	exptl	CBS-QB3	W1X-1(UMP2)	W1X-1(ROMP2)	W2
$Si(OEt)_4$	−1356.0 ± 6.0	−1345.7	−1337.7	−1330.9	−1331.4
$O(SiMe_3)_2$	−777.4 ± 6.0	−756.2	−760.0	−755.0	−761.0
$NH(SiMe_3)_2$	−477.0 ± 5.0	−454.0	−472.0	−457.5	−460.8

[a]Experimental data are taken from the two most recent compilations by Becerra and Walsh.[5,6]

Table 3. Thermochemical Benson Group Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), Entropies (S°_{298K}, J K^{-1} mol^{-1}), and Heat Capacities (C_p, J K^{-1} mol^{-1}) Derived from Results of W1X-1(ROMP2) calculations

Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p\,298K}$	$C_{p\,500K}$	$C_{p\,1000K}$	Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p\,298K}$	$C_{p\,500K}$	$C_{p\,1000K}$
$Si-(C)(H)_3$	20	156	32	45	63	$Si-(C_D)(H)(O)_2$	−4	−35	27	35	39
$Si-(C_D)(H)_3$	36	149	28	45	64	$Si-(F)(H)(O)_2$	−421	71	43	52	58
$Si-(H)_3(O)$	39	151	30	44	63	$Si-(C)_4$[a]	−43	−85	35	33	26
$Si-(H)_3(Si)$	41	152	35	49	68	$Si-(C)_3(O)$[a]	−43	−85	35	33	26
$Si-(C)_2(H)_2$	0	72	31	40	51	$Si-(C)_3(C_D)$	−29	−87	30	32	26
$Si-(C_D)_2(H)_2$	31	53	25	40	52	$Si-(C)_3(Si)$	−11	−86	36	35	30
$Si-(H)_2(O)_2$	11	56	31	41	51	$Si-(C)_2(C_D)_2$	−15	−106	27	31	27
$Si-(H)_2(Si)_2$	39	68	36	46	59	$Si-(C)_2(O)_2$	−53	−104	35	33	27
$Si-(C)(C_D)(H)_2$	16	63	28	40	51	$Si-(C_D)_2(O)_2$	−19	−124	32	39	35
$Si-(C)(H)_2(O)$	11	63	30	39	50	$Si-(C)(C_D)_3$	−2	−116	24	31	28
$Si-(C)(H)_2(Si)$	26	69	34	43	55	$Si-(C)(O)_3$	−57	−108	36	35	29
$Si-(C_D)(H)_2(O)$	28	53	26	39	51	$Si-(C)(C_D)(O)_2$	−35	−111	28	31	26
$Si-(F)(H)_2(O)$	−380	159	38	52	68	$Si-(F)_3(O)$	−1222	214	59	71	78
$Si-(C)_3(H)$	−20	−8	32	36	38	$Si-(F)_2(O)_2$	−840	87	50	57	60
$Si-(C_D)_3(H)$	24	−34	21	34	40	$Si-(O)_4$	−67	−132	43	38	30
$Si-(H)(O)_3$	−30	−34	36	39	40	$C-(C)(H)_2(Si)$	−9	34	22	32	50
$Si-(C)_2(C_D)(H)$	−6	−16	28	35	39	$C-(C)_2(H)(Si)$	18	−59	19	28	39
$Si-(C)_2(H)(O)$	−16	−12	32	36	38	$O-(H)(Si)$	−318	117	14	22	29
$Si-(C_D)_2(H)(O)$	14	−38	25	36	40	$O-(C)(Si)$	−240	39	5	9	16
$Si-(F)_2(H)(O)$	−808	178	47	60	72	$O-(Si)_2$	−416	38	10	17	26
$Si-(C)(C_D)_2(H)$	8	−26	26	36	40	ring strain, 6-membered ring	21	87	−5	−3	−3
$Si-(C)(H)(O)_2$	−22	−26	32	37	39	ring strain, 8-membered ring	4	104	4	5	5

[a]Values for the group $Si-(C)_3(O)$ have been fixed to those of $Si-(C)_4$.

Table 4. Thermochemical Benson Group Pair Contributions for Standard Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}), Entropies (S°_{298K}, J K^{-1} mol^{-1}), and Heat Capacities (C_p, J K^{-1} mol^{-1}) Derived from Results of W1X-1 Calculations

Benson group	$\Delta_f H^\circ_{298K}$	S°_{298K}	$C_{p\,298K}$	$C_{p\,500K}$	$C_{p\,1000K}$
$Si-(C_B)(H)_3 + C_B-(C_B)_2(Si)$	62	104	35	58	83
$Si-(C)(C_B)(H)_2 + C_B-(C_B)_2(Si)$	40	37	39	57	74
$Si-(C_B)(H)_2(O) + C_B-(C_B)_2(Si)$	54	31	44	62	80
$Si-(C_B)_2(H)_2 + C_B-(C_B)_2(Si)$	79	−3	49	74	98
$Si-(C)_2(C_B)(H) + C_B-(C_B)_2(Si)$	17	−47	41	53	62
$Si-(C_B)(C_D)_2(H) + C_B-(C_B)_2(Si)$	46	−65	36	53	63
$Si-(C_B)(H)(O)_2 + C_B-(C_B)_2(Si)$	18	−63	41	53	62
$Si-(C)(C_B)(C_D)(H) + C_B-(C_B)_2(Si)$	31	−60	37	52	62
$Si-(C)(C_B)(H)(O) + C_B-(C_B)_2(Si)$	23	−53	40	53	62
$Si-(C)_3(C_B) + C_B-(C_B)_2(Si)$	−6	−118	44	50	50
$Si-(C)_2(C_B)_2 + C_B-(C_B)_2(Si)$	30	−167	55	68	73
$Si-(C_B)_2(O)_2 + C_B-(C_B)_2(Si)$	22	−182	52	66	73
$Si-(C)_2(C_B)(C_D) + C_B-(C_B)_2(Si)$	7	−135	40	49	50
$Si-(C)(C_B)(C_D)_2 + C_B-(C_B)_2(Si)$	20	−147	38	50	51
$Si-(C)(C_B)(O)_2 + C_B-(C_B)_2(Si)$	−14	−143	45	52	53
$Si-(C_B)(C_D)(O)_2 + C_B-(C_B)_2(Si)$	1	−154	55	70	74
$2*Si-(C)_3(N) + N-(H)(Si)_2$	−204	−134	93	98	96

show, however, greater variation with respect to the original W1X-1(UMP2) data. This is to be expected because they are derived from enthalpies calculated for bigger molecules with aromatic substituents. Overall, the revised values reported herein are the most accurate ones determined to date and we recommend their use in all estimations of thermochemical properties of organosilicon species using Benson's methodology.

The data reported in Tables 3 and 4 were used to estimate the standard enthalpies of formation of organosilicon species examined experimentally by Voronkov et al.[9−14] An updated

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Table 5. Comparison between Experimental (exptl) and Estimated (Benson) Standard Gas Phase Enthalpies of Formation ($\Delta_f H^\circ_{298K}$, kJ mol^{-1}) of Organosilicon Compounds Studied by Voronkov et al.[a]

chemical formula	Benson groups[b,c]	$\Delta_f H^\circ_{298K}$ exptl	$\Delta_f H^\circ_{298K}$ Benson	diff
$SiH(C_4H_9)_3$	6*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−341.0	−298	**43**
$SiH(C_5H_{11})_3$	9*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−402.0	−359	**43**
$SiH(C_6H_{13})_3$	12*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−466.0	−421	**45**
$SiH(C_7H_{15})_3$	15*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−529.0	−483	**46**
$SiH(C_8H_{17})_3$	18*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−591.0	−545	**46**
$SiH(C_9H_{19})_3$	21*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−651.0	−607	**44**
$SiH(C_{10}H_{21})_3$	24*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−713.0	−669	**44**
$SiH(s\text{-}C_4H_9)_3$	6*C−(C)(H)$_3$, 3*C−(C)$_3$(H), 3*tert., 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−355.0	−311	**44**
$SiH(i\text{-}C_5H_{11})_3$	6*C−(C)(H)$_3$, 3*C−(C)$_2$(H)$_2$, 3*C−(C)$_3$(H), 3*tert., 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−413.0	−373	**40**
$SiH(CH_3)(C_4H_9)_2$	4*C−(C)$_2$(H)$_2$, 2*C−(C)(H)$_3$, C−(H)$_3$(Si), 2*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−283.0	−247	**36**
$SiH(CH_3)(C_5H_{11})_2$	6*C−(C)$_2$(H)$_2$, 2*C−(C)(H)$_3$, C−(H)$_3$(Si), 2*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−325.0	−289	**36**
$SiH(CH_3)(C_6H_{13})_2$	8*C−(C)$_2$(H)$_2$, 2*C−(C)(H)$_3$, C−(H)$_3$(Si), 2*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−366.0	−330	**36**
$SiH(CH_3)(C_{10}H_{21})_2$	16*C−(C)$_2$(H)$_2$, 2*C−(C)(H)$_3$, C−(H)$_3$(Si), 2*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−531.0	−495	**36**
$SiH(C_2H_5)(C_4H_9)_2$	4*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−301.0	−256	**45**
$SiH(C_2H_5)(C_5H_{11})_2$	6*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−340.0	−298	**42**
$SiH(C_2H_5)(C_6H_{13})_2$	8*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−381.0	−339	**42**
$SiH(C_2H_5)(C_8H_{17})_2$	12*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−468.0	−421	**47**
$SiH(C_2H_5)(C_{10}H_{21})_2$	16*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_3$, 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−545.0	−504	**41**
$SiH(C_2H_5)(s\text{-}C_4H_9)_2$	5*C−(C)(H)$_3$, 2*C−(C)$_3$(H), 2*tert., 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−315.0	−265	**50**
$SiH(C_2H_5)(i\text{-}C_5H_{11})_2$	5*C−(C)(H)$_3$, 2*C−(C)$_2$(H)$_2$, 2*C−(C)$_3$(H), 2*tert., 3*C−*(C)(H)$_2$(Si)*, *Si−(H)(C)$_3$*	−358.0	−306	**52**
$Si(C_3H_7)_2(C_4H_9)_2$	6*C−(C)$_2$(H)$_2$, 4*C−(C)(H)$_3$, 4*C−*(C)(H)$_2$(Si)*, *Si−(C)$_4$*	−423.0	−372	**51**
$Si(C_3H_7)(C_4H_9)_3$	7*C−(C)$_2$(H)$_2$, 4*C−(C)(H)$_3$, 4*C−*(C)(H)$_2$(Si)*, *Si−(C)$_4$*	−444.0	−392	**52**
$Si(C_3H_7)_2(OC_2H_5)_2$	4*C−(C)(H)$_3$, 2*C−(C)$_2$(H)$_2$, 2*C−(C)(H)$_2$(O), 2*C−*(C)(H)$_2$(Si)*, 2*O−*(C)(Si)*, *Si−(C)$_2$(O)$_2$*	−852.0	−827	**25**
$Si(OC_3H_7)_4$	4*C−(C)(H)$_3$, 4*C−(C)$_2$(H)$_2$, 4*C−(C)(H)$_2$(O), 4*O−*(C)(Si)*, *Si−(O)$_4$*	−1397.0	−1410	**−13**
$Si(OC_4H_9)_4$	8*C−(C)$_2$(H)$_2$, 4*C−(C)(H)$_3$, 4*C−(C)(H)$_2$(O), 4*O−*(C)(Si)*, *Si−(O)$_4$*	−1482.0	−1493	**−11**
$(OSiPh_2)_3$	30*C$_B$−(C$_B$)$_2$(H), 3*[*Si−(C$_B$)$_2$(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], 3*O−(Si)$_2$, 6-member*	−880.0	−747	**133**
$(OSiMe_2)_4$	8*C−(H)$_3$(Si), 4*Si−(C)$_2$(O)$_2$, 4*O−(Si)$_2$, 8-member*	−2138.0	−2210	**−72**
$(OSiMe_2)(OSiPh_2)_3$	30*C$_B$−(C$_B$)$_2$(H), 2*C−(H)$_3$(Si), 4*O−(Si)$_2$, 3*[*Si−(C$_B$)$_2$(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], Si−(C)$_2$(O)$_2$, 8-member*	−1454.0	−1317	**137**
$(OSiMe_2)_2(OSiPh_2)_2$	20*C$_B$−(C$_B$)$_2$(H), 4*C−(H)$_3$(Si), 4*O−(Si)$_2$, 2*Si−(C)$_2$(O)$_2$, 2*[*Si−(C$_B$)$_2$(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], 8-member*	−1691.0	−1615	**76**
$(OSiMe_2)_3(OSiPh_2)$	10*C$_B$−(C$_B$)$_2$(H), 6*C−(H)$_3$(Si), 4*O−(Si)$_2$, 3*Si−(C)$_2$(O)$_2$, [*Si−(C$_B$)$_2$(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], 8-member*	−1910.0	−1912	**−2**
$(OSiPh_2)_4$	40*C$_B$−(C$_B$)$_2$(H), 4*[*Si−(C$_B$)$_2$(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], 4*O−(Si)$_2$, 8-member*	−1226.0	−1020	**206**
$(OSiMePh)_4$	4*C−(H)$_3$(Si), 20*C$_B$−(C$_B$)$_2$(H), 4*[*Si−(C)(C$_B$)(O)$_2$*+ C$_B$−(C$_B$)$_2$(Si)], 4*O−(Si)$_2$, 8-member*	−1685.0	−1609	**76**
$Si(OCH_3)_3[(CH_2)_2SCH_3]$	3*C−(H)$_3$(O), C−(C)(H)$_2$(S), C−(H)$_3$(S), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−946.6	−933	**15**
$Si(OCH_3)_3[(CH_2)_3SCH_3]$	3*C−(H)$_3$(O), C−(C)$_2$(H)$_2$, C−(C)(H)$_2$(S), C−(H)$_3$(S), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−957.0	−954	**5**
$Si(OCH_3)_3[(CH_2)_2S(CH_2CH_3)]$	3*C−(H)$_3$(O), 2*C−(C)(H)$_2$(S), C−(H)$_3$(C), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−962.2	−956	**8**
$Si(OCH_3)_3[(CH_2)_3S(CH_2CH_3)]$	3*C−(H)$_3$(O), 2*C−(C)(H)$_2$(S), C−(C)$_2$(H)$_2$, C−(H)$_3$(C), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−979.9	−977	**5**
$Si(OCH_2CH_3)_3[(CH_2)_2S(CH_2CH_3)]$	4*C−(C)(H)$_3$, 3*C−(C)(H)$_2$(O), 2*C−(C)(H)$_2$(S), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−1069.0	−1055	**16**
$Si(OCH_2CH_3)_3[(CH_2)_3S(CH_2)_3CH_3]$	4*C−(C)(H)$_3$, 3*C−(C)$_2$(H)$_2$, 3*C−(C)(H)$_2$(O), 2*C−(C)(H)$_2$(S), S−(C)$_2$, 3*O−(C)(Si), C−(C)(H)$_2$(Si), Si−(C)(O)$_3$*	−1119.0	−1115	**4**

[a]See refs 9−14 for details of the experimental work. [b]Literature values (kJ mol^{-1}): C−(C)(H)$_3$ = C−(H)$_3$(O) = C−(H)$_3$(Si) = −42.26, C−(C)$_4$ = 19.2, C−(C)$_3$(H) = −1.17, C−(C)$_2$(H)$_2$ = −20.63, C$_B$−(C$_B$)$_2$(H) = −13.81, C−(C)(H)$_2$(O) = −32.90, C−(C)(H)$_2$(S) = −23.17, S−(C)$_2$ = 46.99, tertiary corr = −2.26. [c]Determined in this work (*italicized*, kJ mol^{-1}): C−(C)$_2$(H)(Si) = 18, C−(C)(H)$_2$(Si) = −9, Si−(C)$_4$ = −43, Si−(C)$_3$(H) = −20, Si−(C)$_2$(O)$_2$ = −53, [Si−(C)(C$_B$)(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)] = −14, [Si−(C$_B$)$_2$(O)$_2$ + C$_B$−(C$_B$)$_2$(Si)] = 22, Si−(C)(O)$_3$ = −57, Si−(C)(H)(O)$_2$ = −22, Si−(O)$_4$ = −67, O−(C)(Si) = −240, O−(Si)$_2$ = −416, 6-member ring corr = 21, 8-member ring corr = 4.

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version of Table S4 published in the Supporting Information of our original paper is presented herein as Table 5. The reported values reproduce the same trends as discussed earlier: a systematic difference of around 40 kJ mol^{-1} is seen in the data for tri- and tetrasubstituted alkylsilanes, wildly varying data are observed for longer-chain alkoxysilanes and phenyl-substituted cyclosiloxanes, and excellent harmony between experimental and estimated enthalpies of formation is noted for trimethoxy- and triethoxysilanes with thioether substituents. Thus, we reiterate our earlier conclusion that the data reported by Voronkov et al. should be flagged in thermochemical databases and treated with caution.

As a last note, while comparing our atomic reference energies to those reported in the original W1X-1 work, we noticed that the protocol for the determination of extrapolation exponents α for ΔCCSD and Δ(T) energy components had not been described in detail.[2] A later publication by the same author, however, confirmed that the exponents were determined simultaneously by fitting the energies to the G2/97 set of thermochemical quantities.[15] Although this leads to excellent performance based on the reported benchmark data, it does allow the ΔCCSD and Δ(T) energy components to compensate for one another in a manner that might not work equally well for all possible molecular systems. Consequently, it is entirely possible that the differences between W1X-1 and CBS-QB3 values noted by us (see above) are not entirely due to deficiencies in the latter method but can also be affected by the extrapolation exponents α used in the former. More detailed investigations of the performance of W1X-1 method with respect to the original W1 and W2 variants are currently underway.

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