Ab Initio Predictions for Thermochemical Parameters for Tin−Oxygen Compounds

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Heats of formation have been determined for the tin−oxygen compounds SnO, SnO_2, H_2SnO, and H_3SnOH by ab initio computations of reaction energies for isogyric reactions. The electronic structure methods employed include the coupled-cluster singles and doubles method with a perturbative correction for connected triple substitutions [CCSD(T)] and the Brueckner doubles method with analogous corrections for triple and quadruple substitutions [BD(TQ)]. Correlation-consistent triple- and quadruple-ζ basis sets were employed in conjunction with a large-core pseudopotential and a core polarization potential for Sn, and a basis set incompleteness correction was computed from extrapolations to the infinite basis set limit. Values of 9 ± 4, 10 ± 4, 34 ± 4, and −20 ± 4 kcal mol^{-1} are proposed for $\Delta H^\circ_{\mathrm{f},0}$ for SnO, SnO_2, H_2SnO, and H_3SnOH, respectively. Polynomial fits were carried out for the heat capacity and the standard enthalpy and entropy over the 300−3100 K temperature range.

1. Introduction

The thermochemistry of gas-phase tin compounds containing oxygen is rather poorly characterized. Although standard reference sources[1,2] and critical reviews[3,4] contain data for a few species (typically only SnO and SnO_2), data for hydroxides, organometallics[5] containing oxygen ligands, and small-molecule intermediates are virtually nonexistent. Accurate data for oxygen-containing tin compounds are needed to develop models describing the chemical vapor deposition (CVD) of tin oxide (SnO_2), a transparent conducting oxide used as a low-emissivity coating on architectural glass and in thin-film solar cells, electrochromic windows, and liquid-crystal displays. Tin oxide is produced on an industrial scale by continuous on-line CVD on hot flat glass.[6,7] These processes are extremely complex and difficult to optimize, leading to the need for detailed understanding of the gas-phase chemistry occurring above the deposition surface.

The scant thermochemical data available for tin compounds containing oxygen have been determined experimentally, and we are aware of no ab initio studies of the thermochemistry of tin−oxygen compounds, although a few studies report ab initio bond energies for Sn−X bonds (X = C, Si, Ge, Sn, Pb, Cl) for various other tin-containing species.[8−10] Our laboratory at Sandia has previously made extensive use of ab initio methods to generate thermochemical data for a wide range of main-group compounds, including ones containing boron,[11,12] carbon,[13] nitrogen,[13] aluminum,[14,15] silicon,[12,16−23] gallium,[14,24] and indium.[14] The methods used in these calculations are based on the bond-additivity correction (BAC) approach using fourth-order Møller−Plesset perturbation theory, in which empirically derived corrections are used to obtain accurate heats of formation.[21] These corrections rely, in part, on the availability of established heats of formation for representative reference compounds in a chemical system. For many molecular systems, including tin−oxygen compounds, such data are not available, and high-level ab initio methods may instead be employed to obtain a reference heat of formation of which the value is considered sufficiently accurate that it can provide the basis for establishing the necessary corrections. We used this approach in the past for determining corrections for both Si−O[18] and B−N[11] bonds.

In the present work, we compute thermochemical parameters for four important small molecules containing tin and oxygen: SnO, SnO_2, H_2SnO, and H_3SnOH. SnO and SnO_2 were chosen because they are included in various compilations of thermodynamic data that are in wide use. Thermodynamic properties for SnO are thought to be well-known, so calculating the heat of formation for this molecule provides an opportunity to evaluate the performance of the theoretical approaches used here. H_2SnO was chosen because it is the simplest unsaturated tin−oxygen compound that could be a stable species (in contrast with SnO and SnO_2, which most likely have short lifetimes and exist only at high temperatures) and is also an analogue of compounds that may be important in the CVD of tin oxide. Similarly, H_3SnOH is the simplest four-coordinate tin compound having a Sn−O single bond. Calculation of its heat of formation will permit corrections for such bonds to be established in the BAC method (we are unaware of any experimental data for this compound). We compute heats of formation for these four tin−oxygen species by means of high-level ab initio methods, employing coupled-cluster and Brueckner correlation models in conjunction with correlation-consistent basis sets and a relativistic effective core potential for Sn. Additionally, we provide thermodynamic data over a range of temperatures and polynomial coefficients in the CHEMKIN format,[25] so that the information can be used by others in the modeling of CVD and other high-temperature processes.

2. Computational Details

The heat of formation of SnO was obtained from the reactions

$$SnO + 3H_2 \rightarrow SnH_4 + H_2O \qquad (1)$$

$$SnO + Cl_2 + H_2 \rightarrow SnCl_2 + H_2O \qquad (2)$$

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TABLE 1: Thermochemical Data (kcal mol^{-1}) Employed in the Determination of $\Delta H^\circ_{f,0}$ for Tin−Oxygen Species

species	$\Delta H^\circ_{f,0}$[a]	ZPVE
SnO	5.66 ± 0.96[b]	1.17[b,c]
SnO_2		2.59[d]
H_2SnO		8.69[d]
H_3SnOH		20.87[d]
SnH_4	38.9 ± 0.5[e]	16.08[d]
$SnCl_2$	-48.0 ± 1.7[b]	1.17[d]
H_2	0.0	6.21[c,f]
H_2O	-57.103 ± 0.001[f]	13.25[c,g]
Cl_2	0.0	0.80[c,f]

[a] All values are experimental results. [b] Reference 49. [c] Computed as $\sum_i {}^1/_2\omega_i - \sum_{i\leq j} {}^1/_4 x_{ij}$ using experimentally obtained harmonic vibrational frequencies and anharmonicity constants. [d] Computed from ab initio harmonic vibrational frequencies (see text for details). [e] Reference 5. [f] Reference 47. [g] Reference 56.

and determination of $\Delta H^\circ_{f,0}(SnO_2)$ proceeded via the reactions

$$SnO_2 + H_2 \rightarrow SnO + H_2O \tag{3}$$

$$SnO_2 + 4H_2 \rightarrow SnH_4 + 2H_2O \tag{4}$$

$$SnO_2 + Cl_2 + 2H_2 \rightarrow SnCl_2 + 2H_2O \tag{5}$$

$\Delta H^\circ_{f,0}(H_2SnO)$ was computed from

$$H_2SnO \rightarrow SnO + H_2 \tag{6}$$

$$H_2SnO + 2H_2 \rightarrow SnH_4 + H_2O \tag{7}$$

$$H_2SnO + Cl_2 \rightarrow SnCl_2 + H_2O \tag{8}$$

and for H_3SnOH the reactions

$$H_3SnOH + H_2 \rightarrow SnH_4 + H_2O \tag{9}$$

$$H_3SnOH + Cl_2 \rightarrow SnCl_2 + H_2O + H_2 \tag{10}$$

were employed. Reactions 1−10 are all isogyric and include only small species, so high-level ab initio computations are feasible. The reaction products SnO, SnH_4, and $SnCl_2$ were chosen because their heats of formation are known with a higher accuracy than that of most other small tin compounds, although the uncertainty in these numbers is not negligible, see Table 1. Isogyric reactions were employed in preference to atomization reactions because we believe the isogyric reactions to produce more accurate heats of formation, even though there is a larger uncertainty in the employed experimental $\Delta H^\circ_{f,0}$ values than in the atomic $\Delta H^\circ_{f,0}$ values. Heats of formation computed from atomization energies are also reported for comparison. We note that, to ensure independence of reactions 3−5 and of reactions 6−8, we use the experimental, rather than the computed, value for $\Delta H^\circ_{f,0}(SnO)$ in reactions 3 and 6. We then obtain a set of independent reactions to use for each individual species for which $\Delta H^\circ_{f,0}$ is determined, but there are still dependencies among reactions 1−10 taken as a whole. Thus, for example, the difference between reactions 1 and 2 equals that between the pairs 4−5, 7−8, and 9−10, and the difference in heats of formation predicted by these pairs of reactions will therefore be the same, provided that the same level of theory is employed.

The correlation-consistent basis sets cc-pVXZ[26,27] [X = T (triple), Q (quadruple)] for chlorine, oxygen, and hydrogen and the SDB-cc-pVXZ (X = T, Q) sets[28] for tin were employed. The SDB-cc-pVXZ sets use the large-core Stuttgart−Dresden−Bonn relativistic effective core potential (46 core electrons). Core-valence correlation and static core polarization effects for Sn were estimated by inclusion of a core polarization potential.[29] The effect of correlating the chlorine 2s2p orbitals was investigated using the core-valence correlation-consistent basis set cc-pwCVTZ.[30] In the following, we will use the basis set notation (X, Y) to indicate that the basis set X was used for Sn, and the set Y for other atoms.

The electronic structure methods employed are the Hartree−Fock (HF) method,[31,32] second-order Møller−Plesset (MP2) perturbation theory,[33] fourth-order Møller−Plesset perturbation theory including single, double, and quadruple substitutions [MP4(SDQ)],[34] the coupled-cluster singles and doubles method[35,36] (CCSD), the CCSD method augmented with a perturbative contribution from connected triple substitutions [CCSD(T)],[37] and the Brueckner doubles (BD) method with analogous corrections for triple and quadruple substitutions [BD(T), BD(TQ)].[38,39]

Stationary points were located, and harmonic vibrational frequencies were computed at the MP2 or CCSD(T) level using the (SDB-cc-pVTZ,cc-pVTZ) and (SDB-cc-pVQZ,cc-pVQZ) basis sets. At the CCSD(T) level, gradients and vibrational frequencies were computed using finite difference procedures, whereas analytical first and second derivatives were computed at the MP2 level. Unless otherwise noted, the core orbitals were frozen in all correlated computations (1s on O and 1s2s2p on Cl), and all virtual orbitals were included in the correlation space. The computations including the core polarization potential were performed with MOLPRO,[40] and the Gaussian 98 program suite[41] was used for all other computations.

Extrapolations to the infinite basis set limit were carried out for the Hartree−Fock and correlation energies, using for the Hartree−Fock energies the exponential form[42,43]

$$E^{\mathrm{HF}}_X = E^{\mathrm{HF}}_\infty + A\exp(-BX) \tag{11}$$

where X is the highest angular momentum represented in the basis set, and using for the correlation energies the two-point formula[44]

$$E^{\mathrm{corr}}_\infty = \frac{X^3 E^{\mathrm{corr}}_X - (X-1)^3 E^{\mathrm{corr}}_{X-1}}{X^3 - (X-1)^3} \tag{12}$$

employing two basis sets with cardinal numbers $X - 1$ and X.

For reactions 1−10, reaction energies were computed and used in conjunction with the thermochemical data listed in Table 1. The reaction energies for reactions 1−8 were obtained by means of the focal-point method,[45] which here entails direct computation of (SDB-cc-pVTZ,cc-pVTZ) BD(TQ) reaction energies to which a (SDB-cc-pVTZ,cc-pVTZ) → ∞ CCSD(T) shift is appended as a basis set incompleteness correction. The ∞ basis set results were obtained from extrapolations of the (SDB-cc-pVTZ,cc-pVTZ) and (SDB-cc-pVQZ,cc-pVQZ) energies using eqs 11 and 12 for the HF and correlation energies, respectively. For reactions 9 and 10, the focal-point method involved direct computation of (SDB-cc-pVTZ,cc-pVTZ) CCSD(T) energies to which a (SDB-cc-pVTZ,cc-pVTZ) → ∞ MP4(SDQ) shift was added. (The focal-point procedure employed for reactions 1−8 could not be used for reactions 9 and 10 because computation of (SDB-cc-pVTZ,cc-pVTZ) BD(TQ) and (SDB-cc-pVQZ,cc-pVQZ) CCSD(T) energies for H_3SnOH was not possible with Gaussian 98.)

All reaction energies were corrected for core-valence correlation effects. For Sn, this effect (as well as static core polarization) was estimated as the change in CCSD(T) reaction

TABLE 2: Geometries and Harmonic Vibrational Frequencies Employed in the Determination of $\Delta H^\circ_{f,0}$ for Tin−Oxygen Species[a]

SnO	$r_e = 1.8271^b$; $\omega_e = 822.4^c$
SnO_2	$r_e = 1.8175^b$; $\omega_e = 135, 138, 716, 826^d$
H_2SnO^e	$r_e = 1.8410, 1.7238$; $\alpha = 124.3^d$
	$\omega_e = 441, 444, 720, 774, 1849, 1853^d$
H_3SnOH^f	$r_e = 1.9753, 1.7124, 1.7013, 0.9606^g$
	$\alpha = 113.1, 109.4, 103.6, 110.1, 112.1^g$
	$\omega_e = 114, 516, 522, 596, 746, 747, 764,^g$ 870, 1923, 1939, 1977, 3889^g
SnH_4	$r_e = 1.7072^b$
	$\omega_e = 714(3), 756(2), 1892(3), 1914^d$
$SnCl_2$	$r_e = 2.3802$; $\alpha = 98.3^d$
	$\omega_e = 123, 339, 354^d$
H_2	$r_e = 0.7416^b$
	$\omega_e = 4401.21^h$
H_2O	$r_e = 0.9552$; $\alpha = 104.4^b$
	$\omega_e = 1648.47, 3832.17, 3942.53^i$
Cl_2	$r_e = 2.0030^b$
	$\omega_e = 559.7^h$

[a] Bond distances r_e in Å, bond angles α in deg, and harmonic vibrational frequencies ω_e in cm^{-1}. [b] (SDB-cc-pVQZ,cc-pVQZ) CCSD(T) result. [c] Experimental result from ref 49. [d] (SDB-cc-pVTZ,cc-pVTZ) CCSD(T) result. [e] Bond distances listed in order r_e(Sn−O), r_e(Sn−H); bond angle given is α(H−Sn−O). [f] Bond distances listed in order r_e(Sn−O), r_e(Sn−H_s), r_e(Sn−H), r_e(O−H); bond angles listed in order α(Sn−O−H), α(O−Sn−H_s), α(O−Sn−H), α(H_s−Sn−H_s'), α(H_s−Sn−H); C_s symmetry, H_s, and H_s' are symmetry equivalent. [g] (SDB-cc-pVTZ,cc-pVTZ) MP2 result. [h] Experimental result from ref 47. [i] Experimental result from ref 56.

TABLE 3: Evaluation of $\Delta H^\circ_{f,0}$(SnO)[a]

	cc-pVTZ	cc-pVQZ	∞
Reaction 1: $SnO + 3H_2 \rightarrow SnH_4 + H_2O$			
ΔE_e[HF]	−58.13	−58.62	−58.74
δ[CCSD]	+17.32	+16.53	+15.95
δ[CCSD(T)]	+7.59	+7.67	+7.73
δ[BD(TQ)]	−4.16	[−4.16]	[−4.16]
ΔE_e[corr]	−37.38	[−38.59]	[−39.23]
$\Delta E_0 = \Delta E_e[fp] + \Delta[ZPVE] + \Delta[core]$ $= -39.23 + 9.53 + 3.99 = -25.71$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(SnO) = \Delta H^\circ_{f,0}(SnH_4) + \Delta H^\circ_{f,0}(H_2O) - \Delta E_0$ $= 38.9 - 57.103 + 25.71 = \mathbf{7.51}$ kcal mol^{-1}			
Reaction 2: $SnO + Cl_2 + H_2 \rightarrow SnCl_2 + H_2O$			
ΔE_e[HF]	−143.09	−141.41	−141.00
δ[CCSD]	+19.11	+16.53	+14.64
δ[CCSD(T)]	+7.08	+6.84	+6.67
δ[BD(TQ)]	−3.67	[−3.67]	[−3.67]
ΔE_e[corr]	−120.57	[−121.71]	[−123.36]
$\Delta E_0 = \Delta E_e[fp] + \Delta[ZPVE] + \Delta[core]$ $= -123.36 + 6.24 - 0.07 = -117.19$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(SnO) = \Delta H^\circ_{f,0}(SnCl_2) + \Delta H^\circ_{f,0}(H_2O) - \Delta E_0$ $= -48.0 - 57.103 + 117.19 = \mathbf{12.09}$ kcal mol^{-1}			

[a] All entries in kcal mol^{-1}. The SDB-cc-pVXZ sets were employed for Sn and the cc-pVXZ sets for other atoms. The reaction energy is designated Δ*E*, and the symbol δ denotes the increment in the reaction energy relative to the preceding level of theory. The correction obtained by including a core polarization potential on Sn and correlating the Cl 2s2p orbitals is labeled Δ[core]. The increments in brackets are assumed values based on the cc-pVTZ BD(TQ) results. The focal-point reaction energy ΔE_e[fp] is the number in the bottom right-hand corner of each scheme.

energies computed with the (SDB-cc-pVQZ,cc-pVQZ) basis sets upon inclusion of the Sn core polarization potential. Inclusion of the Cl 2s2p orbitals was investigated separately at the CCSD(T) level using the (SDB-cc-pVTZ,cc-pwCVTZ) basis sets. The effect of correlating the Cl core orbitals was found to be a lowering by 0.09 kcal mol^{-1} of the reaction energies for reactions 2, 5, 8, and 10. The computed corrections for Sn and Cl were both added to the reaction energies computed by the focal-point method.

3. Results and Discussion

The employed geometries and frequencies for all species in reactions 1−10 are listed in Table 2. Ab initio bond distances and frequencies generated in the present work were utilized for all species except the diatomics for which experimental frequencies were employed.

For SnH_4 and SnO, experimental bond distances are available, namely, r_e(Sn−H) = 1.6935 ± 0.0084 Å[46] and r_e(Sn−O) = 1.8325 Å.[47] The (SDB-cc-pVQZ,cc-pVQZ) CCSD(T) bond distances, r_e(Sn−H) = 1.707 and r_e(Sn−O) = 1.827 Å, are 0.014 Å longer and 0.005 Å shorter, respectively, than the corresponding experimental bond distances.

The heats of formation of SnO, SnO_2, H_2SnO, and H_3SnOH were computed from reactions 1−10 using the procedure detailed above and the thermochemical data in Table 1. Although, as noted above, some of these reactions may be expressed as linear combinations of others, the computation of the $\Delta H^\circ_{f,0}$ values is detailed for each individual reaction in Tables 3−6 to display the convergence of the focal-point scheme.

Considering first the computation of $\Delta H^\circ_{f,0}$(SnO), detailed in Table 3, reactions 1 and 2 yield values of 7.5 and 12.1 kcal mol^{-1}, respectively. Reaction 1 converges somewhat more rapidly with respect to basis set improvement, but the two reactions display about the same convergence with respect to improvement of the correlation level. Correlation beyond CCSD(T), computed as the CCSD(T) → BD(TQ) shift, accounts for −4.2 and −3.7 kcal mol^{-1} in reactions 1 and 2, respectively. This shift includes the effect of quadruple substitutions and also a CCSD(T) → BD(T) shift of about −0.7 kcal mol^{-1} resulting from reoptimizing the orbitals in the correlation procedure, that is, the CCSD(T), BD(T), and BD(TQ) reaction energies are −33.22, −33.95, and −37.38 and −116.90, −117.66, and −120.57 kcal mol^{-1} for reactions 1 and 2, respectively, obtained with the (SDB-cc-pVTZ,cc-pVTZ) sets. The nonnegligible CCSD(T) → BD(T) shift may be ascribed to inadequacies in the single-reference wave function for SnO, as indicated by the $\mathcal{T}_1$ diagnostic,[48] which assumes a value of 0.042 for SnO. The $\mathcal{T}_1$ diagnostic, computed as the Euclidian norm of the CCSD single-substitution amplitudes, is an indicator for multireference character in the wave function, and a cutoff of 0.02 has been established,[48] beyond which multireference character becomes significant. The diagnostic is well below 0.02 (0.011 or less) for all other species in reactions 1 and 2. The assumption of basis set convergence of the δ[BD(TQ)] correction appears to be justified, considering that the δ[CCSD(T)] value changes by only 0.08 and −0.24 kcal mol^{-1} for reactions 1 and 2, respectively, when going from the triple- to the quadruple-ζ basis. The computed $\Delta H^\circ_{f,0}$ value from reaction 1 (7.5 kcal mol^{-1}) is in significantly better agreement with the experimental value of 5.66 ± 0.96 kcal mol^{-1} than is the value from reaction 2 (12.1 kcal mol^{-1}). Furthermore, the uncertainty in the experimental values employed in reaction 2 are larger than their counterparts in reaction 1. Ascribing more weight to the result from reaction 1, we then advance a value of 9 ± 4 kcal mol^{-1} for $\Delta H^\circ_{f,0}$(SnO).

The heat of formation for SnO_2 was determined from reactions 3−5, yielding $\Delta H^\circ_{f,0}$ (SnO_2) values of 8.4, 10.2, and 14.8 kcal mol^{-1}, respectively. Reaction 3 converges more rapidly with respect to improvement of the correlation treatment and

TABLE 4: Evaluation of $\Delta H^\circ_{f,0}(\mathrm{SnO_2})$[a]

	cc-pVTZ	cc-pVQZ	∞
Reaction 3: $\mathrm{SnO_2 + H_2 \rightarrow SnO + H_2O}$			
ΔE_e[HF]	−85.49	−81.84	−80.96
δ[CCSD]	+13.85	+13.29	+12.89
δ[CCSD(T)]	+4.10	+4.23	+4.32
δ[BD(TQ)]	−0.89	[−0.89]	[−0.89]
ΔE_e[corr]	−68.43	[−65.21]	[−64.63]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -64.63 + 5.62 - 0.80 = -59.81$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{SnO_2}) = \Delta H^\circ_{f,0}(\mathrm{SnO}) + \Delta H^\circ_{f,0}(\mathrm{H_2O}) - \Delta E_0$			
$= 5.66 - 57.103 + 59.81 = \mathbf{8.37}$ kcal mol^{-1}			
Reaction 4: $\mathrm{SnO_2 + 4H_2 \rightarrow SnH_4 + 2H_2O}$			
ΔE_e[HF]	−143.63	−140.47	−139.70
δ[CCSD]	+31.17	+29.82	+28.84
δ[CCSD(T)]	+11.70	+11.90	+12.05
δ[BD(TQ)]	−5.05	[−0.05]	[−0.05]
ΔE_e[corr]	−105.82	[−103.80]	[−103.86]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -103.86 + 15.15 + 3.19 = -85.52$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{SnO_2}) = \Delta H^\circ_{f,0}(\mathrm{SnH_4}) + 2\Delta H^\circ_{f,0}(\mathrm{H_2O}) - \Delta E_0$			
$= 38.9 - (2 \times 57.103) + 85.52 = \mathbf{10.21}$ kcal mol^{-1}			
Reaction 5: $\mathrm{SnO_2 + Cl_2 + 2H_2 \rightarrow SnCl_2 + 2H_2O}$			
ΔE_e[HF]	−228.59	−223.25	−221.95
δ[CCSD]	+32.95	+29.82	+27.53
δ[CCSD(T)]	+11.18	+11.07	+10.99
δ[BD(TQ)]	−4.56	[−4.56]	[−4.56]
ΔE_e[corr]	−189.00	[−186.92]	[−187.99]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -187.99 + 11.86 - 0.87 = -177.00$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{SnO_2}) = \Delta H^\circ_{f,0}(\mathrm{SnCl_2}) + \Delta H^\circ_{f,0}(\mathrm{H_2O}) - \Delta E_0$			
$= -48.0 - (2 \times 57.103) + 177.00 = \mathbf{14.79}$ kcal mol^{-1}			

[a] All entries in kcal mol^{-1}. The SDB-cc-pVXZ sets were employed for Sn and the cc-pVXZ sets for other atoms. The reaction energy is designated ΔE, and the symbol δ denotes the increment in the reaction energy relative to the preceding level of theory. The correction obtained by including a core polarization potential on Sn and correlating the Cl 2s2p orbitals is labeled Δ[core]. The increments in brackets are assumed values based on the cc-pVTZ BD(TQ) results. The focal-point reaction energy ΔE_e[fp] is the number in the bottom right-hand corner of each scheme.

TABLE 5: Evaluation of $\Delta H^\circ_{f,0}(\mathrm{H_2SnO})$[a]

	cc-pVTZ	cc-pVQZ	∞
Reaction 6: $\mathrm{H_2SnO \rightarrow SnO + H_2}$			
ΔE_e[HF]	−23.97	−21.66	−21.10
δ[CCSD]	−1.26	−1.14	−1.04
δ[CCSD(T)]	−1.89	−1.86	−1.84
δ[BD(TQ)]	+1.93	[+1.93]	[+1.93]
ΔE_e[corr]	−25.19	[−22.72]	[−22.05]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -22.05 - 1.31 - 3.12 = -26.48$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{H_2SnO}) = \Delta H^\circ_{f,0}(\mathrm{SnO}) - \Delta E_0$			
$= 5.66 + 26.48 = \mathbf{32.14}$ kcal mol^{-1}			
Reaction 7: $\mathrm{H_2SnO + 2H_2 \rightarrow SnH_4 + H_2O}$			
ΔE_e[HF]	−82.10	−80.28	−79.84
δ[CCSD]	+16.05	+15.39	+14.91
δ[CCSD(T)]	+5.70	+5.81	+5.89
δ[BD(TQ)]	−2.23	[−2.23]	[−2.23]
ΔE_e[corr]	−62.57	[−61.30]	[−61.27]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -61.27 + 8.22 + 0.87 = -52.18$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{H_2SnO}) = \Delta H^\circ_{f,0}(\mathrm{SnH_4}) + \Delta H^\circ_{f,0}(\mathrm{H_2O}) - \Delta E_0$			
$= 38.9 - 57.103 + 52.18 = \mathbf{33.98}$ kcal mol^{-1}			
Reaction 8: $\mathrm{H_2SnO + Cl_2 \rightarrow SnCl_2 + H_2O}$			
ΔE_e[HF]	−167.06	−163.07	−162.09
δ[CCSD]	+17.84	+15.39	+13.60
δ[CCSD(T)]	+5.19	+4.98	+4.83
δ[BD(TQ)]	−1.73	[−1.73]	[−1.73]
ΔE_e[corr]	−145.76	[−144.42]	[−145.39]
$\Delta E_0 = \Delta E_e[\mathrm{fp}] + \Delta[\mathrm{ZPVE}] + \Delta[\mathrm{core}]$			
$= -145.39 + 4.93 - 3.19 = -143.65$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(\mathrm{H_2SnO}) = \Delta H^\circ_{f,0}(\mathrm{SnCl_2}) + \Delta H^\circ_{f,0}(\mathrm{H_2O}) - \Delta E_0$			
$= -48.0 - 57.103 + 143.65 = \mathbf{38.55}$ kcal mol^{-1}			

[a] All entries in kcal mol^{-1}. The SDB-cc-pVXZ sets were employed for Sn and the cc-pVXZ sets for other atoms. The reaction energy is designated ΔE, and the symbol δ denotes the increment in the reaction energy relative to the preceding level of theory. The correction obtained by including a core polarization potential on Sn and correlating the Cl 2s2p orbitals is labeled Δ[core]. The increments in brackets are assumed values based on the cc-pVTZ BD(TQ) results. The focal-point reaction energy ΔE_e[fp] is the number in the bottom right-hand corner of each scheme.

displays the smallest CCSD(T) → BD(TQ) shift, namely, −0.89 kcal mol^{-1}. The $\mathcal{T}_1$ diagnostic of 0.036 for $\mathrm{SnO_2}$ indicates that a single-reference treatment also for this molecule is somewhat inadequate, although the relatively small correlation increments observed in reaction 3 suggest that the correlation errors of $\mathrm{SnO_2}$ and SnO cancel to a large degree. We then propose a value of 10 ± 4 kcal mol^{-1} for $\Delta H^\circ_{f,0}(\mathrm{SnO_2})$, again ascribing less weight to the result from the reaction involving $\mathrm{SnCl_2}$. A value of $\Delta H^\circ_{f,0}(\mathrm{SnO_2}) = 3.6 \pm 12$ kcal mol^{-1} has previously been determined experimentally.[49]

For $\mathrm{H_2SnO}$, the heats of formation computed from reactions 6−8 are 32.1, 34.0, and 38.6 kcal mol^{-1}. As for $\mathrm{SnO_2}$, the reaction producing SnO, reaction 6, displays the smallest correlation increments. The $\mathcal{T}_1$ diagnostic for $\mathrm{H_2SnO}$ is sizable, 0.036; in fact, $\mathcal{T}_1$ is large for all of the investigated tin species that have a Sn−O double bond. Weighting the results from reactions 6 and 7 more heavily, we arrive at a value of $\Delta H^\circ_{f,0}(\mathrm{H_2SnO}) = 34 \pm 4$ kcal mol^{-1}. To our knowledge the heat of formation for $\mathrm{H_2SnO}$ has not previously been published.

The heats of formation predicted for $\mathrm{H_3SnOH}$ from reactions 9 and 10 are −21.3 and −16.9 kcal mol^{-1}, respectively. In both cases, reaction energies converge rapidly with respect to improved correlation treatment, justifying the lower-level focal-point method that disregards correlation beyond the CCSD(T) level. Additionally, the small $\mathcal{T}_1$ values (0.012 for $\mathrm{H_3SnOH}$ and smaller values for other species) for all species in reactions 9 and 10 suggest that correlation beyond CCSD(T) is negligible. Again weighting the result from the reaction involving $\mathrm{SnCl_2}$ lower, we then estimate a value of −20 ± 4 kcal mol^{-1} for $\Delta H^\circ_{f,0}(\mathrm{H_3SnOH})$. We are not aware of any previously published values for the heat of formation of $\mathrm{H_3SnOH}$, but our result agrees well with a recently computed value[50] of $\Delta H^\circ_{f,0}(\mathrm{H_3SnOH}) = -20.8$ kcal mol^{-1} obtained using the BAC−MP4 method.[51,52]

For comparison with the heats of formation determined from isogyric reactions, $\Delta H^\circ_{f,0}$ values were also obtained from atomization energies computed at the CCSD(T) level using the (SDB-cc-pVQZ,cc-pVQZ) basis including the core polarization potential on Sn. These numbers did not include corrections for basis set incompleteness and correlation beyond CCSD(T). The $\Delta H^\circ_{\mathrm{f},0}$ values computed from the atomization energies are 6.5, 11.3, 40.2, and −16.6 kcal mol^{-1} for SnO, $\mathrm{SnO_2}$, $\mathrm{H_2SnO}$, and $\mathrm{H_3SnOH}$, respectively. These values are in reasonable agreement with the values of 9, 10, 34, and −20 kcal mol^{-1} obtained above from isogyric reactions. Computation of $\Delta H^\circ_{f,0}$ for $\mathrm{SnH_4}$ and $\mathrm{SnCl_2}$ was also performed using the same procedure and yielded values of 41.2 and −47.0 kcal mol^{-1}, respectively, in good agreement with the employed experimental values of 38.9 and −48.0 kcal mol^{-1}. The $\Delta H^\circ_{f,0}$ values computed from atomiza-

TABLE 6: Evaluation of $\Delta H^\circ_{f,0}$(H_3SnOH)[a]

	cc-pVTZ	cc-pVQZ	∞
Reaction 9: $H_3SnOH + H_2 \rightarrow SnH_4 + H_2O$			
ΔE_e[HF]	−4.53	−3.49	−3.23
δ[MP2]	+6.44	+6.46	+6.47
δ[MP4(SDQ)]	−3.12	−3.04	−2.97
δ[CCSD(T)]	+0.62	[+0.62]	[+0.62]
ΔE_e[corr]	−0.58	[0.56]	[0.88]
$\Delta E_0 = \Delta E_e[\text{fp}] + \Delta[\text{ZPVE}] + \Delta[\text{core}]$			
$= 0.88 + 2.25 + 0.00 = 3.13$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(H_3SnOH) = \Delta H^\circ_{f,0}(SnH_4) + \Delta H^\circ_{f,0}(H_2O) - \Delta E_0$			
$= 38.9 - 57.103 - 3.13 = -\mathbf{21.33}$ kcal mol^{-1}			
Reaction 10: $H_3SnOH + Cl_2 \rightarrow SnCl_2 + H_2O + H_2$			
ΔE_e[HF]	−89.49	−86.27	−85.49
δ[MP2]	+1.34	−0.05	−1.07
δ[MP4(SDQ)]	+3.82	+3.56	+3.37
δ[CCSD(T)]	+0.06	[+0.06]	[+0.06]
ΔE_e[corr]	−84.27	[−82.71]	[−83.13]
$\Delta E_0 = \Delta E_e[\text{fp}] + \Delta[\text{ZPVE}] + \Delta[\text{core}]$			
$= -83.13 - 1.04 - 4.06 = -88.23$ kcal mol^{-1}			
$\Delta H^\circ_{f,0}(H_3SnOH) = \Delta H^\circ_{f,0}(SnCl_2) + \Delta H^\circ_{f,0}(H_2O) - \Delta E_0$			
$= -48.0 - 57.103 + 88.23 = -\mathbf{16.87}$ kcal mol^{-1}			

[a] All entries in kcal mol^{-1}. The SDB-cc-pVXZ sets were employed for Sn and the cc-pVXZ sets for other atoms. The reaction energy is designated ΔE, and the symbol δ denotes the increment in the reaction energy relative to the preceding level of theory. The correction obtained by including a core polarization potential on Sn and correlating the Cl 2s2p orbitals is labeled Δ[core]. The focal-point reaction energy ΔE_e[fp] is the number in the bottom right-hand corner of each scheme. The increments in brackets here are assumed values based on the cc-pVTZ CCSD(T) result.

tion energies included atomic spin−orbit corrections for Sn, O, and Cl.[53,54]

For the investigated tin−oxygen compounds, polynomial fits were made for the heat capacity (C_p), enthalpy ($H°$), and entropy ($S°$) as a function of temperature. Fits were carried out over two separate temperature ranges, 300−1100 and 1100−3100 K, using C_p, $H°$, and $S°$ values computed at 100 K intervals. These fits can be used with the CHEMKIN software package[25] and are defined by

$$\frac{C_p}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \tag{13}$$

$$\frac{H^\circ}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T} \tag{14}$$

$$\frac{S^\circ}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7 \tag{15}$$

where $H^\circ = H^\circ(T) - H^\circ(298) + \Delta H^\circ_f(298)$, $\Delta H^\circ_f(298)$ is the species heat of formation at 298 K, $H°(T)$ is the standard enthalpy at temperature T, and $H°(298)$ is the standard enthalpy at 298 K. Note that $H°$ as defined above is the enthalpy used in the CHEMKIN package and that $H°$ does not represent an enthalpy of formation. The fitted coefficients are available on the World Wide Web[55] and may also be obtained from the authors.

Heats of formation were also computed at 298 K, and the resulting changes in the ΔH°_f values [$\Delta H^\circ_f(298) - \Delta H^\circ_f(0)$] are −0.48, −0.57, −1.74, and −3.19 kcal mol^{-1} for SnO, SnO_2, H_2SnO, and H_3SnOH, respectively. The computed temperature correction to thermodynamic properties for H_3SnOH here included all vibrations without correcting for internal rotors. Nevertheless, our 0 → 298 K temperature correction of −3.19 kcal mol^{-1} to ΔH°_f(H_3SnOH) agrees well with the corresponding value[50] of −3.38 kcal mol^{-1} computed with the BAC−MP4 method (which uses HF/6-31G* frequencies scaled by 0.89 and includes a hindered rotor treatment of internal rotation).

4. Concluding Remarks

Heats of formation have been determined for the compounds SnO, SnO_2, H_2SnO, and H_3SnOH by means of high-level ab initio electronic structure methods. Reaction energies for several isogyric reactions were obtained using the focal-point method, which involved computation of (SDB-cc-pVTZ,cc-pVTZ) BD(TQ) [or CCSD(T)] reaction energies to which a (SDB-cc-pVTZ,cc-pVTZ) → ∞ CCSD(T) [or MP4(SDQ)] shift was appended as a basis set incompleteness correction. In the basis set notation (X, Y), X designates the basis set used for Sn and Y the set employed for other atoms. The basis set incompleteness correction was computed from extrapolations of the (SDB-cc-pVTZ,cc-pVTZ), (SDB-cc-pVQZ,cc-pVQZ) energies to the infinite basis set limit. An estimate for the effect of core correlation on tin and chlorine was included, and the final, proposed values for $\Delta H^\circ_{f,0}$ for SnO, SnO_2, H_2SnO, and H_3SnOH are, in order, 9 ± 4, 10 ± 4, 34 ± 4, and −20 ± 4 kcal mol^{-1}. While experimental $\Delta H^\circ_{f,0}$ values of 5.66 ± 0.96 and 3.6 ± 12 kcal mol^{-1} are available for SnO and SnO_2, respectively, the data presented for H_2SnO and H_3SnOH are the first published heats of formation of which we are aware for these species. For all of the investigated tin−oxygen compounds, polynomial fits were carried out for the heat capacity and the standard enthalpy and entropy over the 300−1100 and 1100−3100 K temperature ranges.

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