BAC-MP4 Predictions of Thermochemistry for Gas-Phase Indium Compounds in the In−H−C−O−Cl System

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The BAC-MP4 methodology has been used to calculate the heats of formation and associated thermodynamic parameters for a family of 51 different one-, two-, and three-coordinate indium compounds. The ligands explored were H, CH_3, C_2H_5, OH, OCH_3, and Cl. The BAC-MP4 methodology was calibrated by both experimental data and high-level coupled-cluster calculations. The results agree well with the small amount of published experimental data on InH_n and $InCl_n$ species. A linear variation in compound heats of formation with ligand substitution is identified. For example, the heat of formation gradient, $\Delta(\Delta H_f°)/\Delta n$, in the series $InH_{n-3}Cl_n$ ($n = 0-3$), is −89.6 kcal/mol, with $R = 1.000$. Additionally, trends in bond strengths, bond angles, and bond dissociation energies (BDEs) depending on ligand identity are identified. The BDEs decrease monotonically with increasing atomic number in group III and show similar variations among ligand systems for different metals. These observations and results can be combined with the data from previous studies to guide the selection of CVD precursors and experimental parameters for thin-film deposition of indium-containing materials for semiconductor and optical thin-film applications.

I. Introduction

Chemical vapor deposition (CVD) is commonly used to deposit of a variety of indium-containing thin-film coatings.[1] The materials of greatest interest for industrial applications are indium oxide and the group III−V semiconductors indium nitride, indium phosphide, and indium arsenide. The electrical, optical, and mechanical properties of these materials can be tuned by the use of dopants.[2−4] These materials are frequently used in photovoltaic, electro-optical, and even biological systems.[5−8]

Metal organic and metal halide precursors are used in the deposition of indium-based thin-film materials, such as $In(C_2H_5)_3$ for InP and nonstoichiometric indium-tin-oxide (ITO) growth and $In(CH_3)_3$ for InP and InN formation. Precursors are chosen based upon their vapor pressures and their gas-phase chemistries at temperatures germane to the generation of a specific thin-film crystalline phase with a given orientation, film uniformity, and microcrystalline structure. This chemistry determines whether a precursor will decompose in the gas phase, creating open coordination sites for reaction with other gas-phase reactants or attachment to the growing thin-film lattice. Precursor reactivity is often poorly understood and requires either a trial-and-error approach to selecting precursors or an extension of experimental observations made for adjacent elements in the periodic table. Understanding precursor thermochemistry can also provide guidance to experiment design, both in terms of identifying promising precursor candidates and in terms of selecting deposition conditions and mixtures of reactant gases.

The key thermodynamic quantities for experiment design are the molecular heats of formation of both reactant and product species present in the CVD reactor. From these data, reaction enthalpies and bond dissociation energies (BDEs) can be calculated. Knowledge of the temperature dependence of these quantities is also important for modeling the deposition process, along with the free energy of reaction. Experimental thermodynamic data for InH, InCl, $InCl_2$, $InCl_3$, and InOH have been tabulated separately by Gurvich et al.[9] and the National Bureau of Standards (NBS) tables,[10] while $In(CH_3)_3$ has also been presented[11] and critically appraised.[12,13] Unfortunately, these data represent a small subset of indium species of interest, leading to the necessity of using ab initio quantum mechanical techniques to calculate thermodynamic properties of additional precursor and reactive intermediate species. A study of the InL_n system (L = H, Cl, CH_3; $n = 1-3$) using a combined DFT/coupled-cluster approach has been published,[12,14] as well as a B3LYP-DFT study of a variety of indium species.[15] Neither of these studies were calibrated by experimental data (*vide infra*).

The BAC-MP4 methodology (applying a semiempirical bond additivity correction (BAC) to MP4 calculations) is found to yield accurate heats of formation for a wide range of main group compounds, including hydrocarbons,[16] and compounds of boron,[17] silicon,[18] phosphorus,[19] and tin.[20] These data and those of other BAC-MP4 references therein are collected at the *Thermodynamics Resource* website.[21] The positive results gained from treating other group III[17] and period IV[20] compounds with the BAC-MP4 method give confidence that application of this method to indium species is appropriate. Although higher-level theoretical approaches are feasible for indium compounds,[14] and we use these here to establish corrections for the BAC method, the computational expense of these methods renders them impractical for treating a large number of species.

In this study, the BAC-MP4 method is applied to 51 one-, two-, and three-coordinate indium compounds with the ligands H, CH_3, Cl, C_2H_5, OH, and OCH_3. These include molecules of the form InX_n ($n = 1-3$) as well as $InXY_m$ ($m = 1, 2$) and

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InXYZ, where X, Y, and Z are the six ligands stated previously. The five-coordinate compound, $In(CH_3)_3(H_2O)_2$, and its elimination products, $In(CH_3)_3(H_2O)$ and $In(CH_3)_2(H_2O)_2$, are also studied to test their stability relative to three-coordinate precursor candidates. The molecular geometries, heats of formation, entropies, and free energies of formation are reported in the text, while a complete presentation of computational results, including geometric and vibrational data, and polynomial fits of thermodynamic data suitable for the CHEMKIN suite of reacting-flow codes are found in the Supporting Information. In addition, these data are available as part of the *Thermodynamics Resource*, a website we developed to make available the high-temperature thermochemical data for gas-phase species that result from calculations such as those reported herein.[21] This study also notes the trends in thermodynamic properties of these compounds to permit estimation of thermodynamic data for species not explicitly included in this investigation.

II. Theoretical Methods

II.1. Ab initio Reference Calculations. No suitable heat of formation was found in the literature for compounds including the indium−oxygen bond. This is required to calibrate the BAC correction for molecules possessing such a bond (i.e., indium hydroxide and indium methoxide species). Thus, high-level *ab initio* calculations using the coupled-cluster singles and doubles method with a perturbative correction for connected triple substitutions [CCSD(T)] were performed on $In(OH)_3$ to allow calculation of the BAC parameters for this bond type. Geometries and harmonic vibrational frequencies were computed using the B3LYP density functional method with the cc-pVTZ-PP basis for In[22] and the cc-pVTZ set for other atoms.[23] Single-point energies were computed at these geometries at the CCSD(T) level using the above basis sets and also (when possible) using the cc-pVQZ-PP set for In and the cc-pVQZ set for other atoms. For $In(OH)_3$, where both the TZ and QZ calculations were possible, Hartree−Fock and CCSD(T) correlation energies were extrapolated to the complete basis set limit using extrapolation formulae from the literature.[24,25] Heats of formation were computed from the CCSD(T) energies by means of the following isogyric reaction: $In(OH)_3 + 3H_2 \rightarrow InH_3 + 3H_2O$. The calculated heat of formation is $\Delta H_f(In(OH)_3, 0\ K) = -132.1$ kcal/mol.

II.2. BAC-MP4. The BAC-MP4 method is well developed[26,27] and has been applied previously to molecules containing a number of main-group elements including H, B, C, N, O, F, Al, Si, Cl, and Sn.[16−20] The method, as originally developed, uses the 6-31G(d) (for geometry optimization) and 6-31G(d,p) (for energy calculations) basis sets.[28,29] These apply to elements 1−17 (H−Cl). 6-31G has recently been expanded to the third row (adding elements 18−36, i.e., Ar−Kr),[30] but the BAC-MP4 method has not yet been extended to other elements. Indium is outside of this range, necessitating the use of a different basis set. Consistent with a previous BAC-MP4 study of the Sn−H−C−Cl system,[20] indium is described by the CRENBL-ECP basis set.[31,32] In this basis set, the 1s−4p electrons are described by an effective core potential, while the valence $4d^{10}5s^25p^2$ electrons are modeled with an uncontracted Gaussian basis set containing 3s, 3p, and 4d functions. All calculations in this study were performed using Gaussian 98.[33]

In the BAC-MP4 method, a molecule's equilibrium geometry is determined by Restricted Hartree−Fock (RHF) theory for closed-shell molecules and Unrestricted Hartree−Fock (UHF) for open-shell molecules using a 6-31G(d) basis set (In is described using CRENBL-ECP). The limitations of geometry optimizations performed using a RHF approach are well-known, but it is also recognized that such results give the correct trends within classes of related molecules.[34−37] The resulting structure is verified by calculating the harmonic vibrational frequencies (the absence of imaginary frequencies indicates that the geometry is at a minimum of the potential energy surface). The frequencies, which are used in the subsequent calculation of thermodynamic values, are divided by an empirical scaling factor of 1.12 to account for the systematic overestimation of the vibrational frequencies at this level of theory.[38]

TABLE 1: BAC Parameters for Each Bond, A_{ij} (kcal/mol), and Atom, B_k, Type

	In−H	In−C	In−O	In−Cl	C−C	O−C	C−H	O−H
A_{ij} (MP4)	164.1	528.1	319.1	924.0	1444.1	175.6	38.6	72.5

	In	H	C	O	Cl
B_k (MP4)	0.30	0.00	0.31	0.23	0.42

This geometry is employed in a MP4(SDTQ)/6-31G(d,p) calculation (fourth-order perturbation theory using the 6-31G(d,p) basis set with single, double, triple, and quadruple substitutions) to obtain electronic energies, atomization enthalpies, and by extension, heats of formation. The errors in the calculated heats of formation can be accounted for by empirical bond additivity corrections to deliver final theoretical heats of formation accurate to within a few kcal/mol.

The constituent BAC equations are given below (eq 1−4) for the $X_i−X_j$ bond in the molecule $X_k−X_i−X_j$ and depend on the three parameters, α_{ij}, A_{ij}, and B_k, as well as the length of the bond in question (R_{ij})

$$E_{BAC}(X_i - X_j) = f_{ij}g_{kij} \tag{1}$$

where

$$f_{ij} = A_{ij}\exp(-\alpha_{ij}R_{ij}) \tag{2}$$

$$g_{kij} = (1 - h_{ik}h_{ij}) \tag{3}$$

$$h_{ik} = B_k \exp\{-\alpha_{ik}(R_{ik} - 1.4\ \text{Å})\} \tag{4}$$

$$A_{ij} = (\Delta H_{f,ref}^\circ - \Delta H_{f,calc}^\circ)/(n \exp(-\alpha_{ij}R_{ij})g_{kij}) \tag{5}$$

A_{ij} acts as a reference magnitude for the bond additivity correction (i.e., $E_{BAC}(X_i−X_j) \propto A_{ij}$ from eqs 1 and 2) and is defined as the bondwise-normalized energy difference between the reference ΔH_f° value and the calculated ΔH_f° (eq 5). n is the number of a particular metal−ligand bond type present in the reference molecule (e.g., $n = 3$ as for InH_3 as there are three In−H bonds). α_{ij} is a parameter that depends on the $i−j$ bond type. α_{C-C} is 3.8 $Å^{-1}$, and α_{O-C} is 2.14 $Å^{-1}$ while for all other bond types, α_{ij} is 2.0 Å.[20] B_k (eq 4) corrects for the effects of neighboring atoms on the $X_i−X_j$ bond (eq 3) and depends on the identity of atom k. A_{ij}, α_{ij}, and B_k are specific to the level of theory used for the calculated ΔH_f° value (e.g., A_{ij}(MP4, In−H), using InH_3 as the reference compound for the In−H bond, is $(\Delta H_{f,ref}^\circ(InH_3) - \Delta H_{f,MP4}^\circ(InH_3))/(3 \exp(-\alpha_{ij}R_{ij})g_{kij})$). These parameters are calculated from a set of reference compounds representing each of the bond types present in the set of molecules under investigation. R_{ij} is the bond distance in angstroms. Additional corrections for UHF instability and nonzero ground-state spin are described elsewhere.[26]

Table 1 lists the values of A_{ij} for each bond and B_k for each atom type. To determine BAC parameters for bonds to indium, the calculated MP4(SDTQ) energy was compared to literature heats of formation. The calibrating heats of formation used to determine each indium−ligand bond correction were (kcal/mol) $\Delta H_f°(\mathrm{InH_3}, 0\ \mathrm{K}) = 52.7$,[12,14] $\Delta H_f°(\mathrm{In(CH_3)_3}, 0\ \mathrm{K}) = 24.7$,[12,14] $\Delta H_f°(\mathrm{In(Cl)_3}, 0\ \mathrm{K}) = 87.9$[9], and $\Delta H_f°(\mathrm{In(OH)_3}, 0\ \mathrm{K}) = -132.1$ (*vide supra*). Ligand heats of formation ($\Delta H_f°(298)$) used for BDE calculations were (kcal/mol) H, 52.1; CH_3, 34.9; C_2H_5, 28.8; OH, 9.5; Cl, 29.0; H_2O, −57.8; In, 58.0.[9,20,39]

The sum of the BACs for all bonds in the molecule is added to the MP4(SDTQ) electronic energy and the unscaled zero-point energy to obtain the heats of atomization (ΣD_o) and formation at 0 K and $\Delta H_f°$ (0 K). Through the use of standard expressions from statistical mechanics, $\Delta H_f°$ (0 K), calculated geometries and vibrational frequencies are then combined to calculate the temperature-dependent molecular entropies, heat capacities, enthalpies, and free energies. Unscaled frequencies are used for determining the zero-point energy and $\Delta H_f°$ (0 K), while the scaled frequencies are used to calculate thermochemistry at higher temperatures in order to maintain consistency with earlier papers in this series.[17−20,40−42] The BACs account for the minor differences that would result from using scaled rather than unscaled frequencies to calculate $\Delta H_f°$ (0) as the BACs are calculated from the difference between the MP4 calculated and reference heats of formation (eq 5). Contributions to the heat capacity and entropy from rotating groups are included by substituting a hindered rotor for the corresponding vibrational mode to account for contributions to the heat capacity and entropy from intramolecular rotating groups.[43] The interpolation formulas of Pitzer and Gwinn[44] are used, while the barrier to rotation is determined from the formula reported by Benson[45] for a torsional vibration (calibrated to the barrier reported for the internal rotor in ethane[9] 2.9 kcal/mol)

$$V_0 = I_{\mathrm{red}}\left(\frac{\nu}{134n}\right)^2 \tag{6}$$

V_0 is the barrier height in kcal mol^{-1}, I_{red} is the reduced moment of inertia in amu Bohr^2, ν is the frequency of the internal rotor in cm^{-1}, and n is the rotational symmetry number of the rotating group. A rotational symmetry number of 3 is assigned to the CH_3 groups; all other rotating groups are assigned a value of 2.[46] The hindered-rotor treatment changes $\Delta H_f°$, $S°$, C_p, and $\Delta G_f°$ at temperatures above 0 K relative to treating all vibrations in the same manner. The calculated C_p (300 K) value decreases by 10% for trimethyl indium ($\mathrm{In(CH_3)_3}$) upon inclusion of a hindered rotor treatment, while $S°$ (300 K) decreases by 15% (see Supporting Information for specific values).

Uncertainties in the calculated heats of formation arise from two major sources: (1) uncertainties due to inadequacies of the theoretical methods in describing a given molecule and (2) systematic uncertainties resulting from a paucity of good reference compounds from which to derive the BAC parameters. The first uncertainty is estimated using an ad hoc method developed previously (eq 7) that extrapolates lower-level calculations[26]

$$\begin{aligned}\mathrm{Error(BAC\text{-}MP4)} = {} & \\ & \{1.0\ \mathrm{kcal\ mol^{-1}} + (\Delta H_{\mathrm{BAC-MP4}}° - \Delta H_{\mathrm{BAC-MP3}}°)^2 + \\ & (\Delta H_{\mathrm{BAC-MP4}}° - \Delta H_{\mathrm{BAC-MP4SDQ}}°)^2 + \\ & 0.25(E_{\mathrm{BAC}}(\mathrm{spin}_{S2}))^2\}^{1/2}\end{aligned} \tag{7}$$

The systematic error due to limitations of the experimental reference compound heats of formation scales with the number of bonds in the molecule and can increase the uncertainty estimates by a few kcal/mol. It is important to note that the use of different reference values would offset the entire body of calculated heats of formation, resulting in the calculated BDEs and reaction enthalpies being affected to a smaller degree than the individual heats of formation. Propagating these two independent sources of error through eqs 1−5 and 7 leads to a net uncertainty of ±2.2 kcal/mol for InH_3 and ±3.4 kcal/mol for $\mathrm{In(C_2H_5)_3}$. This result leads us to suggest that the true uncertainty in the heats of formation across the series of molecules presented in this study is on the order of ±2−4 kcal/mol.

BDEs at 298 K were derived from the BAC-MP4 results. The BDE is the heat of reaction for the dissociative reaction $\mathrm{AB} \rightarrow \mathrm{A} + \mathrm{B}$, and yields two uncharged reaction products. When a reaction product is monoatomic or an individual ligand (e.g., CH_3, OH), the experimental heat of formation was used to calculate the bond energy, while for indium-containing polyatomic dissociation products (such as ^{1}InCl) the BAC-MP4 value was used.

III. Results and Discussion

III.1. Bond Lengths and Geometry. Table 2 lists calculated indium-ligand bond lengths and angles for each species, as well as the MP4(SDTQ) BACs corresponding to each bond in the molecule. Internal ligand bond lengths, such as the O−H bond in the OH ligand vary by less than 0.05 Å from their mean values: C−H, 1.086 Å; O−H, 0.947 Å; C−C, 1.530 Å; C−O, 1.389 Å. The indium−ligand bond lengths are also consistent with those reported in the literature[15] and display a standard deviation of less than 2% from the mean value for a particular bond type. The full tabulation of calculated geometries is included in the Supporting Information.

The three-coordinate indium compounds included in this investigation are all planar with respect to the InL_3 unit. The X−In−Y angles vary widely from the symmetric value of 120°, with a maximum of 136° (the C−In−C angle of $\mathrm{In(Cl)(C_2H_5)_2}$) and a minimum of 111° (the O−In−Cl angle of $\mathrm{In(CH_3)(Cl)(OH)}$). The angles follow a consistent trend. X−In−Y angles are smallest if X and/or Y is methoxide, followed by Cl, OH, H, CH_3, and C_2H_5. OCH_3-, Cl-, and OH-containing X−In−Y angles are all within 1° of each other, while H, CH_3, and C_2H_5 are separated by less than 3°. This trend is limited by the three angles summing to 360° and can only be applied to the X−In−Y angles within one molecule. Hence, for $\mathrm{In(CH_3)(Cl)(OH)}$, the angular progression is $\angle(\mathrm{Cl{-}In{-}OH}) < \angle(\mathrm{Cl{-}In{-}CH_3}) < \angle(\mathrm{OH{-}In{-}CH_3})$. The angular variation over the family of indium compounds considered in this study is much greater than those predicted by the HF/6-31G(d) method for tetrahedral tin complexes, using a similar set of ligands.[20] These vary by less than 4.5° from the 109.5° tetrahedral average over a series of 56 molecules.

The geometries of the two-coordinate InXY compounds considered in this study display X−In−Y bond angles ranging from 112° to 120°. The angle is determined by the relative σ- and π-donation properties of X and Y, just as occurs for three-coordinate compounds. The unpaired electron that resides in a p-orbital in the In−X−Y plane causes the two-coordinate compounds to have a bent rather than linear shape.

Additional geometric information, including molecular structures in the form of Cartesian coordinates, moments of inertia, vibrational frequencies, and data concerning hindered rotors are available on the Internet[21] and in the Supporting Information.

III.2. Thermochemical Data. The heats of formation at various levels of theory at 0 K are presented in Table 3 along with reference values from various sources in Table 4. The latter

TABLE 2: In−L Bond Lengths (Å), BACs (kcal/mol), and X−In−Y Angles (deg)

	In−H length	BAC	In−C length	BAC	In−Cl length	BAC	In−O length	BAC	∠1[a]	∠2[a]	∠3[a]
^{1}InH ($^1\Sigma_g$)	1.859	3.99									
^{3}InH	1.763	4.83									
InH_2	1.769	4.77							118.5		
InH_3	1.746	5.00							120.0	120.0	120.0
$^1InCH_3$			2.262	5.73							
$In(CH_3)_2$			2.218	6.23							
$In(CH_3)_3$			2.193	6.52					120.0	120.0	120.0
$In(H)(CH_3)$	1.779	4.67	2.211	6.34					118.0		
$In(H)_2(CH_3)$	1.752	4.94	2.182	6.72					118.5	120.7	120.8
$In(H)(CH_3)_2$	1.759	4.87	2.188	6.62					118.7	118.7	122.7
$^1In(C_2H_5)$			2.274	5.54							
$In(C_2H_5)_2$			2.233	5.98					118.0		
$In(C_2H_5)_3$			2.206	6.28					120.0	120.0	120.0
$In(C_2H_5)H$	1.782	4.65	2.227	6.07					117.5		
$In(C_2H_5)(H)_2$	1.753	4.93	2.195	6.48					120.4	121.1	118.5
$In(H)(C_2H_5)_2$	1.761	4.85	2.200	6.37					119.4	118.7	121.9
^{1}InCl ($^1\Sigma_g$)					2.466	6.66					
^{3}InCl					2.383	7.87					
$InCl_2$					2.377	7.93			115.7		
$InCl_3$					2.326	8.78			120.0	120.0	120.0
In(H)(Cl)	1.773	4.74			2.406	7.52			113.7		
$In(H)_2(Cl)$	1.725	5.21			2.381	7.90			132.0	114.0	114.0
$In(H)(Cl)_2$	1.711	5.36			2.347	8.43			123.2	123.2	113.5
$In(CH_3)(Cl)$			2.239	5.98	2.429	7.16			111.8		
$In(CH_3)_2(Cl)$			2.165	6.87	2.411	7.35			136.3	111.9	111.9
$In(CH_3)(Cl)_2$			2.154	7.05	2.357	8.21			124.0	124.0	112.0
$In(C_2H_5)_2(Cl)$			2.180	6.59	2.414	7.34			136.2	112.1	111.1
			2.182	6.56							
$In(C_2H_5)(Cl)_2$			2.171	6.74	2.362	8.17			111.1	112.7	136.2
					2.360	8.15					
$In(H)(C_2H_5)(Cl)$	1.731	5.15	2.178	6.67	2.398	7.61			133.7	112.0	114.3
^{1}In(OH) ($^1A'$)							2.009	5.74			
$In(OH)_2$							1.986	5.98	112.2		
$In(OH)_3$							1.963	6.22	120.0	120.0	120.0
In(H)(OH)	1.772	4.75					1.992	5.94	120.0		
$In(H)_2(OH)$	1.729	5.16					1.980	6.08	128.9	116.5	114.5
	1.739	5.07									
$In(H)(OH)_2$	1.712	5.35					1.975	6.11	123.0	123.0	114.0
$In(CH_3)(OH)$			2.224	6.16			2.001	5.81	112.0		
$In(CH_3)(OH)_2$			2.153	7.05			1.982	6.00	123.5	123.5	112.9
$In(CH_3)_2(OH)$			2.170	6.82			1.995	5.85	132.1	112.2	115.7
			2.179	6.70							
In(Cl)(OH)					2.386	7.78	1.980	6.06	113.5		
$In(Cl)_2(OH)$					2.324	8.77	1.946	6.45	119.4	120.3	120.3
					2.338	8.53					
$In(OH)_2(Cl)$					2.330	8.66	1.958	6.29	118.3	118.3	123.3
$In(CH_3)(Cl)(OH)$			2.151	7.05	2.383	7.80	1.963	6.23	122.2	127.0	110.8
$^1In(OCH_3)$							2.001	5.67			
$In(H)(OCH_3)$	1.773	4.73					1.991	5.78	112.5		
$In(H)_2(OCH_3)$	1.737	5.09					1.977	5.94	130.4	114.6	114.1
	1.729	5.17									
$In(Cl)(OCH_3)$					2.387	7.77	1.978	5.91	112.8		
$In(Cl)_2(OCH_3)$					2.338	8.54	1.942	6.30	121.0	119.7	119.3
					2.326	8.74					
$In(H)(Cl)(OCH_3)$	1.717	5.30			2.355	8.28	1.955	6.16	121.8	126.5	111.7
$In(CH_3)_3(H_2O)$			2.203	6.39			2.512	2.09	119.6	119.6	119.6
			2.203	6.39							
			2.195	6.49							
$In(CH_3)_2(H_2O)_2$			2.230	6.07			2.728	1.36	117.8	84.9	85.0
							2.727	1.36			
$In(CH_3)_3(H_2O)_2$			2.212	6.27			2.648	1.59	119.3	119.8	120.8
			2.202	6.38			2.649	1.59			
			2.202	6.38							

[a] Angles are ordered according to molecule title, for example, for $In(CH_3)(Cl)(OH)$, $\angle 1 = \angle(CH_3)-In-(Cl) = 122.2°$, $\angle 2 = \angle(CH_3)-In-(OH) = 127.0°$, $\angle 3 = \angle(Cl)-In-(OH) = 110.8°$.

illustrates both the paucity of experimental reference data upon which to base the BAC parameters and the need for thermochemical data for use in choosing experimental conditions and starting materials for the deposition of indium-containing thin films. Values of the atomic heats of formation at 0 K used in this calculation were obtained from the *JANAF Thermochemical Tables*,[39] with the exception of indium, whose value is obtained from Gurvich et al.[9]

$\Delta H_f°(298)$, $S°(298)$, and $\Delta G_f°(298)$ for the 51 molecules investigated in this study are given in Table 5. Polynomial fits of C_p, $S°$, and the enthalpy functions for each compound in the format appropriate for use in CHEMKIN calculations[47] can be

TABLE 3: ΔH_f(0 K) at a Range of Levels of Theory: MP4, BAC-MP2, BAC-MP3, BAC-MP4(SDQ), and BAC-MP4(SDTQ)

	MP4	spin cont.[a]	BAC-MP2	BAC-MP3	BAC-MP4 (SDQ)	BAC-MP4 (SDTQ)
^{1}InH	55.8		53.4	52.3	52.0	51.8
^{3}InH	101.5	0.6	94.5	95.9	95.8	96.0
InH_2	80.4	0.3	70.1	70.6	70.4	70.5
InH_3	67.7		52.7	52.7	52.7	52.7
$^{1}InCH_3$	61.3		43.2	43.1	42.9	42.5
$In(CH_3)_2$	91.6	0.4	51.5	52.5	52.3	52.2
$In(CH_3)_3$	83.9		24.9	24.7	24.7	24.8
$In(H)(CH_3)$	86.1	0.4	60.9	61.6	61.4	61.5
$In(H)_2(CH_3)$	73.4		43.7	43.5	43.5	43.6
$In(H)(CH_3)_2$	78.9		34.5	34.3	34.2	34.3
$^{1}In(C_2H_5)$	74.7		43.5	44.2	44.2	43.1
$In(C_2H_5)_2$	116.3	0.5	50.3	52.7	52.9	51.5
$In(C_2H_5)_3$	122.6		24.7	26.6	27.4	25.4
$In(C_2H_5)H$	98.5	0.5	60.3	61.6	61.6	61.1
$In(C_2H_5)(H)_2$	86.3		43.7	44.2	44.3	43.8
$In(C_2H_5)_2(H)$	104.6		34.3	35.4	35.8	34.7
^{1}InCl	−8.3		−15.0	−14.5	−14.3	−15.0
^{3}InCl	69.5		59.1	60.9	61.0	61.2
$InCl_2$	−13.2	0.3	−30.9	−29.4	−29.3	−29.5
$InCl_3$	−61.4	0.4	−87.8	−87.9	−87.9	−87.7
In(H)(Cl)	31.6		17.4	18.7	18.7	18.6
$In(H)_2(Cl)$	21.3	0.7	2.4	2.8	2.9	3.0
$In(H)(Cl)_2$	−21.8		−44.5	−44.2	−44.1	−44.0
$In(CH_3)(Cl)$	34.2		5.2	6.9	6.7	6.6
$In(CH_3)_2(Cl)$	28.1	1.1	−19.9	−19.7	−19.6	−19.5
$In(CH_3)(Cl)_2$	−20.3		−57.3	−57.3	−57.2	−57.0
$In(C_2H_5)_2(Cl)$	53.2		−20.7	−19.0	−18.5	−19.7
$In(C_2H_5)(Cl)_2$	−8.2		−58.3	−57.3	−56.9	−57.5
$In(H)(C_2H_5)(Cl)$	37.2		−9.1	−8.2	−7.9	−8.4
^{1}In(OH)	−9.2		−25.3	−24.1	−25.0	−25.9
$In(OH)_2$	−22.6	0.7	−57.9	−55.6	−56.5	−57.1
$In(OH)_3$	−80.6		−131.9	−132.1	−132.1	−132.0
In(H)(OH)	27.4	0.6	4.5	6.3	5.5	5.2
$In(H)_2(OH)$	16.5		−10.8	−10.2	−10.6	−10.7
$In(H)(OH)_2$	−33.2		−72.8	−72.4	−72.5	−72.6
$In(CH_3)(OH)$	31.2	0.9	−6.6	−4.5	−5.4	−5.8
$In(CH_3)(OH)_2$	−29.8		−84.0	−83.8	−84.0	−84.0
$In(OH)(CH_3)_2$	25.0		−31.6	−31.4	−31.8	−31.8
In(Cl)(OH)	−18.9	0.6	−45.3	−43.3	−43.8	−44.2
$In(Cl)_2(OH)$	−69.5		−103.9	−103.9	−104.0	−104.0
$In(OH)_2(Cl)$	−73.9		−116.8	−116.9	−117.0	−117.1
$In(CH_3)(Cl)(OH)$	−27.2		−72.7	−72.4	−72.5	−72.5
$^{1}In(OCH_3)$	10.3		−16.3	−14.8	−16.2	−17.3
$In(H)(OCH_3)$	48.2	0.6	14.8	16.8	15.6	15.2
$In(H)_2(OCH_3)$	37.4		−0.5	0.3	−0.4	−0.7
$In(Cl)(OCH_3)$	1.9	0.6	−35.0	−32.5	−33.5	−34.1
$In(Cl)_2(OCH_3)$	−47.9		−93.0	−92.4	−93.0	−93.2
$In(H)(Cl)(OCH_3)$	−6.3		−47.9	−47.2	−47.7	−47.9
$In(CH_3)_3(H_2O)$	36.3		−44.9	−46.9	−46.6	−46.3
$In(CH_3)_2(H_2O)_2$	5.0	0.3	−79.0	−80.2	−79.9	−79.9
$In(CH_3)_3(H_2O)_2$	−7.0		−109.8	−112.9	−112.4	−112.6

[a] "Spin cont." is the spin contamination contribution of excited states into the ground state that is present in open-shell molecules calculated using the UHF method. All values are in kcal/mol.

found in the Supporting Information and on the Internet.[21] BDEs are found in Table 6 for the reaction A−B → A + B. These are derived from the BAC-MP4 calculated $\Delta H_f°(298)$ values for indium-containing compounds and literature values for ligands.

Comparison with Literature Heats of Formation. Comparing experimental and computational heats of formation, $\Delta H_f°(298)$, for gas-phase indium species is difficult due to the small body of experimental data available. The NBS tables report the heats of formation for $InCl_3$, InCl, and InH,[10] while Gurvich provides these three species in addition to $InCl_2$ and InOH.[9] The correlation between these values and the BAC-MP4 prediction is strong for InH, InOH, and InCl (within 0.2, 2.9, and 2.7 kcal/mol, respectively). The reported $InCl_2$ heat of formation (−48.0 kcal/mol) is 18.2 kcal/mol lower than the BAC-MP4 value. This difference is quite large; however, the literature value is an estimate drawn from correlations with $InCl_3$ and MX_2 species (M = B, Al; X = H, Cl), leading to the 25% error estimate on the reported value. No meaningful comparison of the experimental and BAC-MP4 $InCl_3$ heats of formation can be made as this compound was used as a reference for the BAC of the In−Cl bond.

The experimental heats of formation have also been published for $In(CH_3)_3$ (41.1,[48] 41.4±1.5,[49] 40.8±1.5,[11] and 47.9[12] kcal/mol). These values originate from one reported experiment,[48] the heat of reaction of $In(CH_3)_3$ with liquid bromine to form $In(Br)_3$ and CH_3Br, but vary depending upon the heats of formation selected for the other reactants and products in the reaction. Each of these values is 20 kcal/mol greater than the BAC-MP4 value, which is based upon a CCSD(T) calculation (*vide supra*). The origin of this difference is not readily apparent, and the veracity of the experimental value can only be verified

TABLE 4: BAC-MP4 ΔH_f(298 K) and Corresponding Literature Values[a]

	$\Delta H_f°$(298) (BAC-MP4)	Allendorf et al., Bauschlicher (CC)[12,14]	Cardelino et al. (B3LYP)[15,53]	Other literature
^{1}InH	51.3	50.61		51.4 ± 0.5[b], 51.5[c]
InH_2	69.3	70.99		
InH_3	50.7	51.76	44.06	
$^1InCH_3$	40.4	40.26	38.92	
$In(CH_3)_2$	48.1	50.21	48.72	
$In(CH_3)_3$	18.7	20.2	24.26	41.4 ± 1.6;[d] 40.8 ± 1.5;[e] 47.9[f]
$In(H)(CH_3)$	58.7		56.01	
$In(H)(CH_3)_2$	29.6		38.60	
^{1}InCl	−15.3	−16.45	−22.65	−17.2 ± 1.2[b], −18[c]
$InCl_2$	−29.9	−30.18		−48.0 ± 12[b]
$InCl_3$	−88.1	−89.32	−100.08	−87.86 ± 2.9,[b] −89.39[c]
^{1}In(OH)	−26.8			−29.74 ± 3.59[b], −18.88[c]

[a] All values are in kcal/mol. [b] Gurvich et al.[9] [c] NBS tables.[10] [d] Reference 49. [e] Reference 11. [f] Reference 12.

with additional experimental data. The high-level CCSD(T) calculation upon which the BAC-MP4 value is based has proved successful at predicting the thermochemistry of other group III (B, Al, Ga)[50,51] and fourth-row elements (Sn,[20] Sb[52]), giving confidence in this value over the experimental value.

Quantum calculations using a wide variety of computational methods have been used to derive various thermochemical properties of InCl, $InCl_3$, InH, InH_2, InH_3, $In(CH_3)H_2$, and $In(CH_3)_3$. These data are well summarized elsewhere[15] and reproduce experimental data with varying degrees of success. Two relatively systematic studies report computed thermochemical data for a range of indium species, using coupled-cluster theory[12,14] and DFT.[15] The coupled-cluster calculations used B3LYP-derived geometries and frequencies, describing indium with the LANL2 basis set and H, C, and Cl by 6-31+G(d). These structures were then applied to CCSD(T) calculations with the cc-pVx (x = TZ, QZ, and 5Z) basis sets to determine energetics. The small set of molecules considered were of the form InX_n, where X = H, CH_3, or Cl and $n = 1$, 2, or 3. The computed heats of formation correlate well with both the experimental data and the BAC-MP4 results (Table 4), with the heats of formation of the nine compounds presented differing by less than 2 kcal/mol from the BAC-MP4 values. This agreement is encouraging as the coupled-cluster and BAC-MP4 approaches use different approximations. Comparing the heats of formation of molecules common to both this BAC-MP4 study and the Cardelino et al. DFT paper[15,53] (InH_3, $InCH_3$, $In(CH_3)_2$, $In(CH_3)_3$, $In(H)(CH_3)$, $In(H)(CH_3)_2$, InCl, and $InCl_3$) identified a similar correlation. The difference in the calculated heats of formation between the two sets varies from −9.0 ($In(H)(CH_3)_2$) to 12.0 kcal/mol ($InCl_3$) (Table 4). The experimental heats of formation of three of these molecules have been reported, with the DFT-calculated heats of formation lower in each case, differing by 5.5 (InCl), 12.2 ($InCl_3$), and 23.6 kcal/mol ($In(CH_3)_3$). The DFT-calculated heat of formation for $In(CH_3)_3$ is 24.3 kcal/mol, in closer agreement with the CCSD(T) value of Bauschlicher[14] (20.2 kcal/mol) than with the experimental value (47.9[12,49]). These calculations used the popular B3LYP functional and 3-21G(d,p), supplemented by the AKR4 extended basis set for indium and 6-311G(d,p) for H, C, and Cl.

Trends in Three-Coordinate Compounds. Variation in the heat of formation upon ligand substitution is of interest to CVD precursor selection as it allows precursors of varying stability to be chosen depending on experimental conditions. A near-linear relationship upon ligand substitution is observed for each of the 12 InX_nY_{3-n} series ($n = 0$, 1, 2, 3, X, Y = Cl, H, CH_3, C_2H_5, OH, or OCH_3) considered in this study, with the Pearson's linear correlation coefficient (R) of greater than 0.99 being calculated in each case. The gradient of the heat of formation vs n (the ligand substitution number, InX_nY_{3-n}) reflects the difference in substitution enthalpy between indium and the ligands being substituted. This is illustrated by the $In(H)_nY_{3-n}$ series (Figure 2) where a positive gradient is observed in each case, indicating that whenever H is substituted for OH, CH_3, Cl, or C_2H_5 in a three-coordinate indium molecule, the heat of formation increases and the molecule becomes less stable. This indicates that the In−H bond is the least stabilizing indium−ligand bond of the ligands considered in this study. In fact, $\Delta H_f°(InH_3)$ is positive (50.7 kcal/mol), indicating that this species is enthalpically unstable with respect to its elemental components. The relative substitution enthalpies to indium can be read directly from Figure 1: In-OH > In−Cl > $In-C_2H_5$ ∼ $In-CH_3$ > In−H. These substitution enthalpies should not be confused with the BDEs (*vide infra*) for the reaction $A-B \rightarrow A + B$. The bond dissociation energy trend may be slightly different as the BDE also depends on the stability of the isolated fragments.

This linearity with ligand substitution extends to the three-molecule series with three different ligands ($InX_nY_{2-n}Z$, $n = 0, 1, 2$) such as $In(H)_2(OCH_3)$, $In(H)(Cl)(OCH_3)$, and $In(Cl)_2(OCH_3)$. The average energy change with each substitution is similar for corresponding InX_nY_{3-n} and $InX_nY_{2-n}Z$ series: for $InCl_{3-n}H_n$, replacing an H ligand with a Cl decreases the heat of formation by 46.2 kcal/mol, while the same substitution in the $In(OCH_3)Cl_{2-n}(H)_n$ series decreases the heat of formation by 45.6 kcal/mol. The difference in this case is only 0.6 kcal/mol and is within 5 kcal/mol for each of the four series considered in this study. This linearity suggests that knowledge of the heats of formation of two members of a InX_nY_{3-n} series, such as $In(OH)_3$ (−87.63 kcal/mol) and $In(Cl)_3$ (−131.9 kcal/mol), allows one to reasonably estimate the difference in the heats of formation of very different molecules. For example, the $\Delta(\Delta H_f)$ between $In(CH_3)(Cl)(OH)$ and $In(CH_3)(Cl)_2$ (i.e., the change in the heat of formation upon substituting Cl for OH in $In(CH_3)(Cl)(OH)$) is calculated to be 14.3 kcal/mol by BAC-MP4 (Table 5) and estimated to be 15.4 by extrapolating from the difference between the heats of formation of $In(OH)_3$ and $In(Cl)_3$.

The BDEs of three-coordinate indium compounds display a clear trend depending on the ligand identity: BDE($In-C_2H_5$) < BDE($In-CH_3$) < BDE(In−H) < BDE($In-OCH_3$) < BDE(In−OH) < BDE(In−Cl) (Figure 2). This confirms the well-known fact that deposition from organometallic precursors, whether controlled by gas-phase or surface chemistry, occurs at lower temperatures than that from halogenated precursors. Conversely, the choice of a Cl- or OH-containing precursor depends largely upon the identities of the other ligands chosen, as the In−Cl BDE of $In(CH_3)_2Cl$ is of less interest because

TABLE 5: $\Delta H_f^\circ(298)$ (with errors), $\Delta S^\circ(298)$, and $\Delta G_f^\circ(T)$ Derived from BAC-MP4 Calculations (energies in kcal/mol, entropies in cal/mol K)

			ΔG_f°(K)					
	ΔH_f° (298)	ΔS° (298)	300	600	1000	1500	2000	2500
^{1}InH	51.3 ± 1.1	49.6	45.2	39.6	33.4	26.0	18.5	11.3
^{3}InH	95.5 ± 1.0	51.6	88.8	82.7	75.7	67.3	58.9	50.7
InH_2	69.3 ± 1.0	56.1	65.9	63.3	60.9	58.2	55.3	52.6
InH_3	50.7 ± 1.0	54.9	52.3	54.7	59.1	64.5	69.6	74.5
$^1InCH_3$	40.4 ± 1.3	64.2	39.7	39.9	41.9	45.1	48.2	51.2
$In(CH_3)_2$	48.1 ± 1.0	81.1	56.8	66.8	82.5	103.1	123.4	143.3
$In(CH_3)_3$	18.7 ± 1.0	92.7	38.3	59.7	90.9	130.9	170.2	208.7
$In(H)(CH_3)$	58.7 ± 1.0	69.3	61.2	64.6	71.1	79.7	88.1	96.4
$In(H)_2(CH_3)$	40.1 ± 1.0	69.9	47.0	55.0	67.4	83.3	98.6	113.5
$In(H)(CH_3)_2$	29.6 ± 1.0	81.3	42.8	57.5	79.3	107.2	134.6	161.3
$^1In(C_2H_5)$	39.6 ± 1.8	73.4	45.8	53.4	65.9	82.4	98.5	114.4
$In(C_2H_5)_2$	44.6 ± 2.1	99.9	67.1	91.8	127.9	174.0	219.4	263.6
$In(C_2H_5)_3$	15.2 ± 2.5	119.9	55.8	99.3	161.4	239.9	316.7	391.3
$In(C_2H_5)H$	56.9 ± 1.3	78.6	66.3	77.1	93.8	115.3	136.5	157.2
$In(C_2H_5)(H)_2$	38.9 ± 1.2	79.3	52.8	68.1	90.7	119.4	147.4	174.7
$In(C_2H_5)_2(H)$	27.2 ± 1.7	100.1	54.3	83.5	125.8	179.2	231.5	282.5
^{1}InCl	−15.3 ± 1.3	59.6	−21.1	−26.4	−32.4	−39.5	−46.5	−53.3
^{3}InCl	60.9 ± 1.1	61.5	54.6	48.7	42.0	34.0	26.1	18.4
$InCl_2$	−29.9 ± 1.0	75.3	−32.4	−34.4	−36.3	−38.3	−40.3	−42.1
$InCl_3$	−88.1 ± 1.0	82.1	−84.6	−81.0	−75.5	−68.6	−62.1	−55.5
In(H)(Cl)	17.8 ± 1.0	67.3	14.3	11.5	8.7	5.5	2.2	−0.9
$In(H)_2(Cl)$	1.3 ± 1.0	66.4	2.8	5.0	8.7	13.5	17.9	22.2
$In(H)(Cl)_2$	−45.1 ± 1.0	75.5	−42.9	−40.4	−36.3	−31.1	−26.2	−21.4
$In(CH_3)(Cl)$	4.4 ± 1.1	79.6	7.1	10.6	17.0	25.5	33.9	42.2
$In(CH_3)_2(Cl)$	−23.7 ± 1.1	90.4	−9.8	5.3	27.5	56.0	83.9	111.3
$In(CH_3)(Cl)_2$	−59.3 ± 1.0	88.2	−51.2	−42.4	−29.3	−12.6	3.8	19.8
$In(C_2H_5)_2(Cl)$	−26.6 ± 1.7	109.0	1.0	30.8	73.5	127.8	181.1	233.3
$In(C_2H_5)(Cl)_2$	−61.2 ± 1.2	97.6	−46.2	−30.1	−6.8	22.8	51.8	80.2
$In(H)(C_2H_5)(Cl)$	−12.8 ± 1.1	88.7	1.5	17.2	40.1	69.2	97.6	125.5
^{1}In(OH)	−26.8 ± 2.2	61.1	−29.1	−30.7	−31.8	−32.7	−33.6	−34.3
$In(OH)_2$	−58.9 ± 1.9	74.2	−53.0	−46.6	−37.0	−24.8	−12.6	−0.4
$In(OH)_3$	−134.7 ± 1.0	82.0	−119.1	−103.1	−81.2	−54.0	−27.2	−0.5
In(H)(OH)	3.5 ± 1.6	66.2	4.4	5.9	9.0	13.1	17.0	21.0
$In(H)_2(OH)$	−13.2 ± 1.1	66.6	−7.7	−1.6	7.5	18.8	29.7	40.4
$In(H)(OH)_2$	−75.1 ± 1.0	74.3	−64.7	−53.6	−38.0	−18.6	0.3	19.2
$In(CH_3)(OH)$	−8.8 ± 1.7	78.3	−1.7	6.3	18.6	34.5	50.2	65.8
$In(CH_3)(OH)_2$	−87.8 ± 1.0	87.4	−71.4	−54.1	−29.7	1.1	31.4	61.4
$In(OH)(CH_3)_2$	−36.8 ± 1.1	89.4	−18.6	0.9	28.9	64.5	99.5	133.9
In(Cl)(OH)	−45.3 ± 1.4	76.1	−44.0	−42.3	−39.0	−34.6	−30.2	−25.7
$In(Cl)_2(OH)$	−105.2 ± 1.0	85.2	−98.6	−91.8	−82.1	−69.9	−58.2	−46.4
$In(OH)_2(Cl)$	−118.8 ± 1.0	84.2	−107.9	−96.6	−80.8	−61.0	−41.6	−22.3
$In(CH_3)(Cl)(OH)$	−75.6 ± 1.0	86.8	−63.1	−49.8	−30.9	−7.0	16.3	39.1
$^1In(OCH_3)$	−19.9 ± 3.0	73.1	−16.0	−10.8	−1.9	10.0	21.8	33.5
$In(H)(OCH_3)$	12.0 ± 2.0	77.0	19.4	28.1	41.4	58.6	75.6	92.3
$In(H)_2(OCH_3)$	−4.6 ± 1.4	76.9	7.6	20.9	40.3	64.9	88.8	112.3
$In(Cl)(OCH_3)$	−36.7 ± 1.1	85.9	−28.6	−19.5	−5.8	11.9	29.3	46.6
$In(Cl)_2(OCH_3)$	−95.8 ± 1.0	95.2	−82.4	−68.4	−48.2	−22.8	2.2	26.8
$In(H)(Cl)(OCH_3)$	−51.1 ± 1.0	86.8	−38.6	−25.1	−5.5	19.2	43.4	67.3
$In(CH_3)_3(H_2O)$	−53.1 ± 1.0	110.2	−22.1	10.7	57.0	115.4	172.8	229.1
$In(CH_3)_2(H_2O)_2$	−85.1 ± 1.3	121.5	−55.3	−24.2	18.9	72.9	125.8	177.7
$In(CH_3)_3(H_2O)_2$	−119.6 ± 1.0	129.7	−77.8	−34.3	26.2	102.0	176.3	249.2

the methyl ligands will dissociate much more readily ($BDE_{298K}((CH_3)(Cl)In-CH_3) = 65.9$ kcal/mol vs $BDE_{298K}((CH_3)_2\text{-}In-Cl) = 103.8$ kcal/mol). It is also worth noting that there is a greater spread in the BDEs for Cl and OH relative to the hydrocarbons, indicating that the magnitude of the BDE becomes more dependent upon the identity of the other ligands in the compound as the BDE increases.

Trends in Two- and One-Coordinate Compounds. The molecules discussed in the previous section can undergo elimination reactions of the type, $InX_3 \rightarrow InX_2 + X$, whose products can then further dissociate to InX + X. The heats of formation do not follow a linear trend upon ligand elimination; $\Delta H_f^\circ(InX_2)$ is greater than the average of $\Delta H_f^\circ(InX_3)$and $\Delta H_f^\circ(InX)$ as can be seen in Table 5. This is in contrast with the linear variation in ΔH_f° upon ligand substitution discussed above. The relatively larger ΔH_f° value of InX_2 translates into a smaller BDE for XIn−X compared to X_2In-X and In−X (Figure 3). This destabilization has been attributed to changes in sp^3 hybridization in analogous Ge compounds[54] and has been observed in a number of systems[20] in addition to the group III compounds shown[12,55,56] (Figure 3). For group IV compounds, this "high-low-high" BDE pattern is known as the "inert pair effect"[57] and is quantified by the reaction enthalpy of the disproportionation reaction, which for indium is

$$2InX_2 \leftrightarrows InX_3 + InX$$

The enthalpies of this reaction for the ligands studied are (kcal/mol) −36.6 (H), −43.7 (Cl), −53.6 (OH), −37.2 (CH_3), and −34.5 (C_2H_5). It is instructive to compare these values with those of other members of group III: B, Al, and Ga. The similarity in the difference of successive BDEs is readily

TABLE 6: In−L Bond Dissociation Energies at 298 K (kcal/mol)

	In−H BDE	In−C BDE	In−Cl BDE	In−O BDE
^{1}InH	58.8			
^{3}InH	14.6			
InH_2	34.1			
InH_3	70.7			
$^{1}InCH_3$		52.5		
$In(CH_3)_2$		27.1		
$In(CH_3)_3$		64.3		
$In(H)(CH_3)$	33.7	27.4		
$In(H)_2(CH_3)$	70.8	64.1		
$In(H)(CH_3)_2$	70.7	64.1		
$^{1}In(C_2H_5)$		47.2		
$In(C_2H_5)_2$		23.7		
$In(C_2H_5)_3$		58.2		
$In(C_2H_5)H$	34.7	23.1		
$In(C_2H_5)(H)_2$	70.1	59.1		
$In(C_2H_5)_2(H)$	69.6	64.7		
^{1}InCl			102.3	
^{3}InCl			26.1	
$InCl_2$			43.5	
$InCl_3$			87.2	
In(H)(Cl)	19.0		62.5	
$In(H)_2(Cl)$	68.5		96.9	
$In(H)(Cl)_2$	67.3		91.8	
In(CH3)(Cl)		15.2	65.0	
$In(CH_3)_2(Cl)$		62.9	100.8	
$In(CH_3)(Cl)_2$		64.3	92.6	
$In(C_2H_5)_2(Cl)$			100.3	
$In(C_2H_5)(Cl)_2$		60.1		
$In(H)(C_2H_5)(Cl)$	75.2	59.3	98.7	
^{1}In(OH)				94.3
$In(OH)_2$				41.6
$In(OH)_3$				85.2
In(H)(OH)	21.8			64.0
$In(H)_2(OH)$	68.8			92.0
$In(H)(OH)_2$	68.3			88.1
$In(CH_3)(OH)$		16.9		58.7
$In(CH_3)(OH)_2$		63.7		88.4
$In(OH)(CH_3)_2$		62.8		94.4
In(Cl)(OH)			47.5	39.5
$In(Cl)_2(OH)$			88.8	84.8
$In(OH)_2(Cl)$			88.8	82.9
$In(CH_3)(Cl)(OH)$		65.1	95.7	89.4
$^{1}In(OCH_3)$				87.4
$In(H)(OCH_3)$	20.2			48.8
$In(H)_2(OCH_3)$	68.6			83.3
$In(Cl)(OCH_3)$			45.7	30.8
$In(Cl)_2(OCH_3)$			88.1	75.4
$In(H)(Cl)(OCH_3)$	66.5		92.0	78.3
$In(CH_3)_3(H_2O)$				14.0
$In(CH_3)_3(H_2O)_2$		69.5		8.8

observed in the nested curves for AlH_n, GaH_n, and InH_n shown in Figure 3. The difference between the BH and BH_2 BDEs is less than that of the other metals indicating a different electronic structure in the boron compounds. Such an inconsistency is anticipated by other physical attributes of these compounds, such as the H−M−H bond angle of MH_2: ∠H−M−H is 119°, 119.5°, and 118.5° for M = Al,[58] Ga,[59] and In, respectively, while ∠H−B−H is 131°.[58] The disproportionation enthalpies of Al−H, Ga−H, and In−H (as defined in the above reaction for In−X) are −39.3, −41.7, and −36.6 kcal/mol, respectively, while that of B−H is −28.1 due to the relatively small BDE of the BH molecule. The InX_2 disproportionation enthalpies are 2−5 kcal/mol greater than those reported for the corresponding PbX and SiX compounds (X = H, CH_3, Cl), although the utility of this comparison is limited as the disproportionation enthalpies for lead and silicon are based on the reaction

$$2MX_3 \leftrightarrows MX_4 + MX_2$$

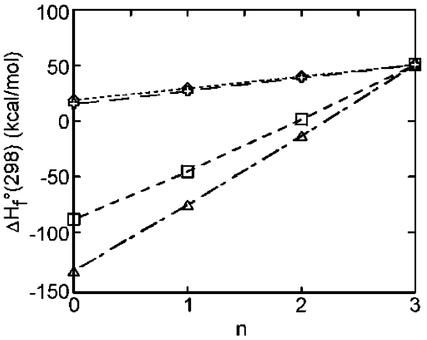

Figure 1. Heats of formation (298 K) for InH_nX_{3-n} ($n = 1-3$, X = OH (triangles), Cl (squares), CH_3 (diamonds), and C_2H_5 (+)—the X = CH_3 and C_2H_5 values are nearly identical). Each series converges at InH_3 (i.e., $n = 3$, $(3 - n) = 0$).

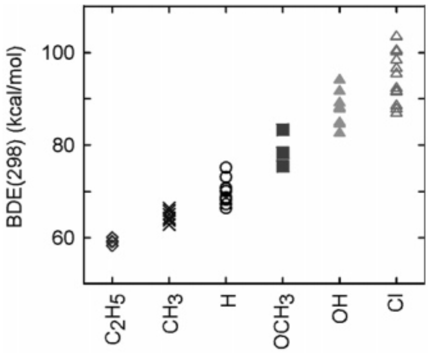

Figure 2. Bond dissociation energies (BDEs) for three-coordinate compounds of the form YZIn−X. X is denoted on the horizontal axis.

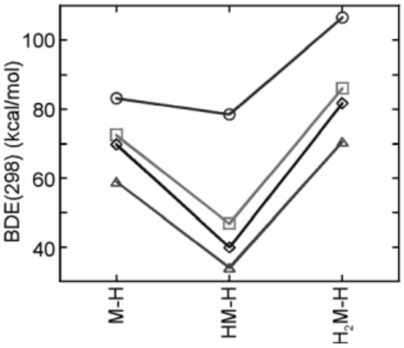

Figure 3. Bond dissociation energies (BDEs) for group III compounds MH_n (M = B (circles), Al (squares), Ga (diamonds), In (triangles), $n = 1-3$) and B, Al, and Ga BDEs from G2 calculations,[12] in BDEs from this work.

An alternative to a sequential ligand dissociation mechanism for CVD precursor decay is molecular elimination of the type

$$InX_3 \rightarrow InX + X_2$$

For X = H, Cl, CH_3, and OH, the heat of reaction for molecular elimination is lower than that of eliminating two individual ligands as $X_2 \rightarrow 2X$ is endothermic for each of these ligands. The heat of reaction for the molecular elimination of H_2 from InH_3 is slightly endothermic ($\Delta H_{rxn}° = 0.6$ kcal/mol), while the double ligand elimination is strongly endothermic ($\Delta H_{rxn}° = 104.8$ kcal/mol). The H_2 elimination reaction is spontaneous at 600 K, $\Delta G_{rxn,600K}° = -15.1$ kcal/mol (Table 5), whereas the sequential ligand elimination is strongly nonspontaneous ($\Delta G_{rxn,600K}° = 74.6$ kcal/mol). A similar analysis can be easily performed for the binary pairs of ligands for molecular elimination reactions from mixed-ligand molecules, InXYZ. However, such a consideration does not address the kinetics of the reaction, which requires knowledge of transition-state energetics and is beyond the scope of the present work, although there are experimental kinetic data available for select reactions.[60]

Another reaction pathway of interest is the β-hydride elimination of ethylene from ethyl-containing indium compounds. For triethyl indium, the reaction products are $In(C_2H_5)_2(H)$ and C_2H_4, with $\Delta H_{rxn}° = 24.3$ kcal/mol.[61] This is much smaller than the heat of reaction of ethyl dissociation from triethyl indium of 58.2 kcal/mol (Table 6). This may be the origin of the greater thermal instability for triethyl indium relative to trimethyl indium[62] even though the two species have similar In−C bond strengths. Again, transition-state energetics will determine the preferred pathway of precursor decomposition.

Both the singlet and triplet states of InH and InCl were calculated to determine which is more stable, with the singlet state preferred in both cases, by 44.2 kcal/mol in InH and 76.2 kcal/mol in InCl, at 298 K. The singlet state is also stable for the other ligands considered in this study (OH, CH_3, C_2H_5, and OCH_3), while the triplet dissociates to $^2In + {}^2L$ during geometry optimization. This indicates that the singlet state is more stable than the triplet state of the dissociating molecules by more than the BDE of $^1(In-X)$ where (X = OH, CH_3, C_2H_5, OCH_3): 94.3, 52.5, 47.2, and 87.4 kcal/mol, respectively.

$In(CH_3)_3(H_2O)_2$. Although much interest exists in elimination reactions of indium compounds and the reactivities of the resulting products for CVD applications, the potential for gas-phase complex formation, particularly via addition reactions, should also be evaluated. The planar, three-coordinate species $In(CH_3)_3$ has two open coordination sites along the 3-fold axis of rotation. The p_z orbital is unoccupied, making it suitable for attack by Lewis bases such as water and ammonia. Water can be used as an oxygen source in oxide film formation[63] and is a common contaminant in CVD reactors[64] due to the hygroscopicity of many metal−organic CVD precursors. The addition of water to trimethyl indium to form $In(CH_3)_3(H_2O)$ is calculated to be exothermic by 14.0 kcal/mol (Table 6), while the addition of a second water molecule to form $In(CH_3)_3(H_2O)_2$ is slightly less exothermic at 8.8 kcal/mol. However, at typical CVD temperatures, such as 600 K, the calculation predicts that the entropic component will dominate reactivity, with $\Delta G_{r,600K}(In(CH_3)_3 + 2(H_2O) \leftrightarrows In(CH_3)_3(H_2O)_2) = 10.0$ kcal/mol, a nonspontaneous reaction. At lower temperatures, the entropic component is less important, but the formation of the five-coordinate species does not become spontaneous until the temperature falls below 400K, and suggests that the five-coordinate species could play a role in lower temperature CVD processes. Similarly, formation of the four-coordinate compound, $In(CH_3)_3(H_2O)$ from trimethyl indium and water, is not spontaneous at 600 K ($\Delta G_r = 3.0$ kcal). However, a substitution reaction, such as $In(CH_3)_3 + (H_2O) \leftrightarrows In(CH_3)_3(H_2O) \leftrightarrows In(CH_3)_2(OH) + CH_4$, is calculated to be spontaneous ($\Delta G_{r,600K} = -12.4$ kcal) and may play a role in metal−organic precursor decomposition.

IV. Summary and Conclusions

Driven by the paucity of experimental data, the heats of formation and associated thermodynamic parameters have been calculated for a family of 51 one-, two-, and three-coordinate indium compounds with H, CH_3, C_2H_5, OH, OCH_3, and Cl ligands. The BAC-MP4 methodology was calibrated by both experimental and high-level coupled-cluster calculations and agreed well with the narrow range of previously published InH_n and $InCl_n$ species.

These results identified linear variations in compound heats of formation with ligand substitution, as well as trends in bond strengths, bond angles, and BDE that depend on ligand identity. The BDEs decrease monotonically down group III but showed similar variations between ligand systems for different metals. These observations and results can be combined with the data from previous studies[16−20,26,27,40−42] to guide the selection of CVD precursors and experimental parameters for the deposition of indium-containing materials.

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Supporting Information Available: Molecular geometries, vibrational data, and Chemkin coefficients of various indium compounds and the effects of including hindered rotor treatment to $In(CH_3)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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