Are the Compounds InH$_3$ and TlH$_3$ Stable Gas Phase or Solid State Species?

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The stability of the group 13 hydrides in the oxidation state +III of the metal is analyzed by ab initio MP2 calculations suggesting that In$_2$H$_6$ and Tl$_2$H$_6$ are thermodynamically unstable in both the gas phase and the solid state. These compounds are, however, kinetically stable in the gas phase, and molecular structures and vibrational frequencies are predicted. Relativistic effects are discussed for the molecular properties of various thallium hydrides.

Introduction

The stability of the group 13 hydrides [MH$_3$]$_n$ (M = B, ..., Tl) has been a matter of considerable interest[1,2] ever since Egon Wiberg claimed the synthesis of some of these species more than 40 years ago.[3,4] According to several authors[2,5,6] it seems unlikely that [InH$_3$]$_n$ and [TlH$_3$]$_n$ are sufficiently stable to be isolated, in contrast to Wiberg's early findings. Only BH$_3$,[7,8] B$_2$H$_6$,[9,10] and very recently AlH$_3$,[11,12] GaH$_3$,[12] Ga$_2$H$_6$,[10] and InH$_3$,[12] have been studied to any extent by spectroscopic methods. There is some evidence for hydride formation when the metals Ga, In, or Tl react with atomic hydrogen.[13] Estimates of bond stabilities have been made,[14] B$_2$H$_6$ has been isolated and well characterized,[4] [AlH$_3$]$_n$ is known as a polymeric solid,[1,15] and solid [GaH$_3$]$_n$ is possibly an oligomer with n = 4.[10] In contrast, the monovalent Group 13 hydrides MH have all been detected in the gas phase and their spectroscopic properties are accurately known.[16] Schaefer et al.[17−19] predicted the vibrational spectra and stability of M$_2$H$_6$, M$_3$H$_9$, and M$_4$H$_{12}$ (M = B, Al, Ga), and it was suggested that Al$_2$H$_6$ may be stable in the gas phase. In general, however, with the exception of boron hydrides,[20] there are few theoretical investigations of the stability of group 13 MH$_3$ compounds or their dimers M$_2$H$_6$.[21−25] To our knowledge, In$_2$H$_6$ and Tl$_2$H$_6$ have not been studied by theoretical methods so far.

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Scheme 1
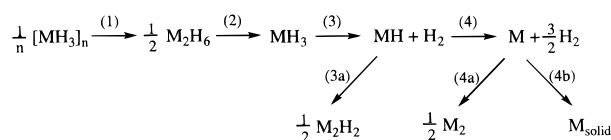
Computational Method

We carried out relativistic (R) Hartree−Fock (HF) and second-order Møller−Plesset (MP2) calculations on a series of group 13 hydrides MH, MH_3 (D_{3h}) and M_2H_6 (C_{2h}) for M = In and Tl.[26] The definition for the terminal (t) and bridged (b) hydrogens in the M_2H_6 structure is as follows:
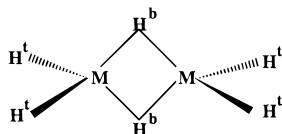
The spin−orbit averaged relativistic pseudopotentials for Tl and In were taken from refs 23 and 27. In order to investigate relativistic effects we also carried out nonrelativistic (NR) pseudopotential calculations for the thallium hydrides using the nonrelativistic parameters published in ref 23. The basis set for indium was an uncontracted (7s/6p/2d) valence set as described in ref 25. For relativistic Tl we used an uncontracted (7s/7p/2d) set, and a (8s/7p/2d) set in the nonrelativistic case. The exponents are given in refs 22 and 23. For H we took a contracted Huzinaga (9s)/[6s] basis set[28] with two p-polarization functions given by Lie and Clementi[29] and a diffuse s-function with exponent 0.01. For Tl_2H_6 this resulted in 172 basis functions contracted to 154 functions making the MP2 calculations very demanding in computer time and disk space.[30] The full active orbital space was taken in all MP2 calculations. The energy differences are corrected for zero-point vibrational-energy contributions (ZPVE) if not otherwise stated.

Discussion

We consider the following reaction steps shown in Scheme 1 important for evaluating both the gas phase and solid state thermodynamic stabilities of the group 13 hydrides. The ΔU_0 values (at 0 K if not otherwise stated) for each reaction (ΔU_0-(1) to ΔU_0(4b)) are listed in Table 1. $\Delta U_0(1)$ is *not* easy to obtain from theoretical calculations, because the solid state structures are not known (except for B_2H_6) and correlated solid state calculations at the ab initio level are only beginning at this stage. However, one may attempt to estimate this energy from the oligomerization energy of the MH_3 compounds calculated recently by Schaefer and co-workers for up to $(MH_3)_4$ (M = B, Al, Ga).[18,19] As shown in Table 1, these energies are rather small in accordance with the low melting points obtained for the group 13 hydrides B_2H_6, $[AlH_3]_n$, and $[GaH_3]_n$[1,4,10] (e.g., allane decomposes before it melts at ca. >150 °C; borane and gallane melt at −165 and −50 °C respectively).[4,10] We should

Table 1. Reaction Energies of all Group 13 Hydrides[a]

M	solid	eq 1[b]	eq 2[c]	eq 3[d]	eq 3a[e]	eq 4[f]	eq 4a[g]	eq 4b[h]	gas
B	(−16)	73	335	−190	118	−146	−560	yes	yes?
Al	100 (6)	65	94	−55	79	−75	−330	yes	yes
Ga	(8)	43	58	−44	58	−68	−277	yes	no?
In		43	2	−52	23	−49	−243	no?	no
Tl		19	−59	−37	−23	(−8)	−182	no	no

[a] In kJ/mol (see Scheme 1). The last two columns are predictions of the thermodynamic stability of $[MH_3]_n$ in the gas phase ($n = 2$) or the solid state ($n = \infty$). If not otherwise indicated, MP2 results were chosen. [b] In parentheses are the estimated values obtained from the additional energy gained by trimerization (see ref 18). [c] Values for B from ref 8, for Al and Ga from ZPVE corrected CCSD/CISD calculations of ref 18. [d] From QCISD(T) calculations (ref 25) corrected for ZPVE. [e] From ref 33 corrected for ZPVE. In the case of B_2H_2 the linear $^1\Sigma_g^+$ state has been chosen; otherwise the doubly hydrogen-bridged structure has been chosen. [f] From ref 16. [g] From ref 16. Estimated value for Tl from ref 36. [h] Atomization energies at 25 °C taken from refs 1, 31, and 39.

mention, however, that these energies are *not* good estimates for the sublimation energy. For AlH_3 the enthalpy of formation is known ($\Delta H_f \approx -46$ kJ/mol)[31] from which we estimate that $\Delta U_0(1)$ is probably around 100 kJ/mol, which is substantial and cannot be neglected. Hence, it seems that AlH_3 is thermodynamically stable in the solid phase. However, $\Delta U_0(1)$ probably decreases down the group 3 hydrides (as does the oligomerization energy from AlH_3 to GaH_3)[19] or may only slightly increase from GaH_3 to InH_3 according to the often observed zigzag trend in molecular properties of group 13 compounds (see discussion in ref 25). We cannot give an estimate for ΔU_0-(1) and will therefore neglect this contribution for a moment.[32]

For the gas phase stability we consider either the decomposition into M_2H_2 (3a) or into the metal dimers M_2 (4a). $\Delta U_0(3a)$ can be estimated from a recent publication by Treboux and Barthelat.[33] These authors also give vibrational frequencies for various M_2H_2 gas phase structures. In_2H_2 and Tl_2H_2 have been investigated before.[34] Figure 1 shows the total energies of these two reactions ($\Delta U_0(2) + \Delta U_0(3) + ...$). In both cases there is a decreasing trend in the gas phase stability from B_2H_6 to Tl_2H_6. This demonstrates, that while gas phase B_2H_6, Al_2H_6, and Ga_2H_6 are thermodynamically stable at lower temperatures (thus neglecting entropy effects which become important at higher temperatures), the decomposition of Tl_2H_6 (and perhaps In_2H_6) is predicted to be exothermic (at any temperature). Table 1 shows that the major reason for this trend is the strong decrease in stability of the MH_3 species from M = B down to M = Tl

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(32) To calculate the solid state structure in order to estimate the cohesive energy of the solid group 13 hydrides would be a rather difficult if not impossible task with the current setup of computer methods. The main reason for this is that accurate electron correlation effects for the interaction between the different dimers or oligomers are very difficult to obtain for the solid state. Currently, weak interactions between molecules are, for example, not well described in density functional theory due to the wrong behavior of the functional at large interatomic distances. Moreover, weak interactions between molecules can only be described in a satisfactory way by using very large basis sets and multireference configuration interaction procedures.

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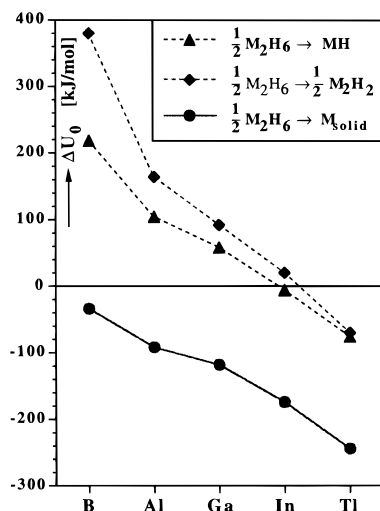
Figure 1. Decomposition energies ΔU_0 for the group 13 M$_2$H$_6$ compounds (M = B, Al, Ga, In and Tl) according to the reactions shown in Scheme 1.

Table 2. MP2 Geometries of Group 13 Hydrides MH and MH$_3$ (M = In, Tl)[a]

		$r_{\text{M}-\text{H}^t}$	$r_{\text{M}-\text{H}^b}$	$r_{\text{M-M}}$	α^t	α^b	ΔU_0
InH	R	1.838					
	exptl	*1.837*					
InH$_3$	R	1.725			120		18.2
In$_2$H$_6$	R	1.710	1.946	2.961	130.2	80.9	100.1
TlH	R	1.896					
	exptl	*1.870*					
	NR	1.924					
TlH$_3$	R	1.728			120		−58.4
	NR	1.831			120		27.9
Tl$_2$H$_6$	R	1.701	2.003	3.063	135.4	80.2	48.8
	NR	1.818	2.036	3.145	129.7	78.8	122.9

[a] M−H bond distances r_e in Å, bond angles α_e in deg. Experimental values are set in parantheses. t denotes the terminal and b the bridging hydrogen. α^t defines the H^t−M−H^t angle and α^b the H^b-M-H^b angle. ΔU_0 in kJ/mol (MH$_3$ → MH + H$_2$ for MH$_3$, and M$_2$H$_6$ → 2MH$_3$ for M$_2$H$_6$; values are not corrected for ZPVE). R denotes the relativistic and NR the nonrelativistic treatment.

Table 3. MP2 Vibrational Frequencies of InH, InH$_3$, TlH, and TlH$_3$[a]

	$\nu_1(A_1')$ sym str	$\nu_2(A_2'')$ out of plane	$\nu_3(E')$ asym str	$\nu_4(E')$ bend
InH	1475 (1018)			
exptl	*1476*			
InH$_3$	1818(0)	642(321)	1784(344)	690(253)
exptl		*608*	*1755*	*613*
TlH	1329(1205)			
exptl		*1391*		
TlH$_3$	1792(0)	673(225)	1741(387)	644(244)

[a] Frequencies in cm^{-1} and absolute IR intensities in km/mol (set in parentheses). Rotational constants (cm^{-1}): InH 4.995 (exp. 4.995, ref 16); InH$_3$ $a = b = 3.748$, $c = 1.874$; TlH 4.677 (exptl 4.806, ref 16); TlH$_3$ $a = b = 3.734$, $c = 1.867$. Isotopes used: ^{1}H, ^{115}In, and ^{205}Tl. Experimental frequencies for InH$_3$ from ref 11.

(see the discussion in ref 25). In$_2$H$_6$ is borderline, and more accurate data are necessary to clearly decide if this compound is thermodynamically stable or not. In$_2$H$_6$ and Tl$_2$H$_6$ are, however, kinetically stable, i.e. a local minimum was found at the MP2 level. It may therefore be feasible to obtain these compounds in matrix isolation or even measure their gas phase structures. For this purpose we predict the geometries, vibrational frequencies and IR intensities as presented in Tables 2−4.

The quality of our calculations can be judged by comparing our data with experimental results for the dimeric compounds

Table 4. MP2 Vibrational Frequencies ν and IR Intensities I of In$_2$H$_6$ and Tl$_2$H$_6$[a]

			In$_2$H$_6$		Tl$_2$H$_6$	
			ν	I	ν	I
IRREP	mode	description	(cm^{-1})	(km/mol)	(cm^{-1})	(km/mol)
A$_g$	ν_1	ν(M−H^t) sym str	1848	0	1842	0
	ν_2	ν(M−H^b)	1372	0	1251	0
	ν_3	δ(M−H$_2^t$)	661	0	628	0
	ν_4	sym ring def	164	0	112	0
A$_u$	ν_5	ρ_t(M−H$_2^t$)	380	0	381	0
B$_{1g}$	ν_6	ν(M−H^b)	1177	0	1051	0
	ν_7	ρ_w(M−H$_2^t$)	350	0	161	0
B$_{1u}$	ν_8	ν(M−H^t)	1837	522	1831	542
	ν_9	ρ_r(M−H$_2^t$)	753	261	708	229
	ν_{10}	ring def	202	10	193	2
B$_{2g}$	ν_{11}	ν(M−H^t)	1831	0	1824	0
	ν_{12}	ρ_r(M−H$_2^t$)	397	0	404	0
B$_{2u}$	ν_{13}	ν(M−H^b)	1089	420	962	472
	ν_{14}	ρ_w(M−H$_2^t$)	588	259	617	164
B$_{3g}$	ν_{15}	δ(M−H$_2^t$)	684	0	667	0
B$_{3u}$	ν_{16}	ν(M−H^t)	1841	139	1839	120
	ν_{17}	ν(M−H^b)	1262	1372	1118	1426
	ν_{18}	δ(M−H$_2^t$)	607	834	526	1073

[a] For details of the normal mode descriptions see Nakamoto.[37] Rotational constants (cm^{-1}): In$_2$H$_6$ $a = 1.307$, $b = 0.032$, $c = 0.032$; Tl$_2$H$_6$ $a = 1.264$, $b = 0.017$, $c = 0.017$. Isotopes used: ^{1}H, ^{115}In, and ^{205}Tl.

InH and TlH. As shown in Tables 2 and 3, the M−H bond distances and stretching frequencies for the dimeric hydrides are in excellent agreement with the experimental values. Recently, Pullumbi et al. studied InH at the all-electron CCSD-(T) level neglecting relativistic effects and obtained a harmonic frequency of 1406 cm^{-1} and a In−H bond distance of $r_e = 1.898$ Å.[38] Hence, our MP2 stretching modes should be quite reliable. However, a comparison with the recently measured vibrational spectrum of InH$_3$ in matrix isolation by Pullumbi et al.[12] shows that our bending modes may be overestimated (Table 3). These authors also give CCSD(T) frequencies of 1706 cm^{-1} (A$_1'$), 1704 and 604 cm^{-1} (E′), and 582 cm^{-1} (A$_2''$). Their measured relative intensities agree very well with our calculated ones. A comparison of the frequencies between MH, MH$_3$, and M$_2$H$_6$ shows that these three species can be clearly distinguished in the IR spectrum.

Concerning the solid state stability, the decomposition of M$_2$H$_6$ is clearly driven by the large atomization energies of the group 13 metals. As a result, solid In$_2$H$_6$ and Tl$_2$H$_6$ are predicted to be thermodynamically unstable ($\Delta U_0(1)$ must be >185 kJ/mol in order to stabilize In$_2$H$_6$ in the solid state which is unlikely). B$_2$H$_6$ is perhaps borderline, and more accurate thermodynamic data, especially for reaction 1, are necessary to draw further conclusions. The energies given for reaction 4b are atomization enthalpies at 298 K. In order to estimate the 0 K values we can use the approximation $\Delta U_0 \approx \Delta H_f^{298} - 298C_p$ (C_p: specific heat capacity). We find, however, that these corrections are negligible (<8 kJ/mol taking the C_p values from ref 39). At higher temperatures entropy effects could substantially shift all curves shown in Figure 1 to lower energies. We therefore calculated the entropy changes of reactions 2 and 3 from statistical thermodynamics methods (at 298K) using the vibrational-rotational constants as listed in Tables 3 and 4 (in J

(38) Pullumbi, P.; Mijoule, C.; Manceron, L.; Bouteiller, Y. *Chem. Phys.* **1994**, *185*, 13.
(39) (a) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverund, A. N. JANAF Thermochemical Tables, 3rd ed. *J Phys. Chem. Ref. Data* **1985**, *14*. (b) Brewer, L.; Rosenblatt, G. M. *Adv. High Temp. Chem.* **1969**, *2*, 1.

Hunt and Schwerdtfeger

mol^{-1} K^{-1}): $\Delta S(2)= -95$ and $\Delta S(3)= -109$ for M = In; $\Delta S(2)= -124$ and $\Delta S(3)= -110$ for M = Tl. Applying these data, In$_2$H$_6$ is found to be thermodynamically stable only at low temperatures. The synthesis of gallane is less than a straight forward procedure.[1] We therefore conclude that isolating [InH$_3$]$_n$ and [TlH$_3$]$_n$ in solid form would be an even more difficult task compared to [GaH$_3$]$_n$, and the original synthesis described by Wiberg remains very doubtful.

The low thermodynamic stability of Tl$_2$H$_6$ can partly be attributed to relativistic effects, i.e. compare the relativistic and nonrelativistic decomposition energies listed in Table 2. The relativistic destabilization of TlH$_3$ is ca. 86 kJ/mol at the MP2 level! Remarkable is the very large relativistic bond angle change of $\Delta_R\alpha = 5.7°$ in the H^t−Tl−H^t angle of the terminal hydrogens. This is unusual since relativistic effects in bond angles are assumed to be quite small.[35] The MP2 Mulliken atomic charges for In and Tl show an interesting trend: $+0.43$ for InH, $+0.89$ for InH$_3$, and $+1.10$ for In$_2$H$_6$; $+0.41$ ($+0,42$) for TlH, $+0.96$ ($+1.15$) for TlH$_3$, and $+1.08$ ($+1.33$) for Tl$_2$H$_6$ (nonrelativistic values set in parentheses). Hence, the hydrogens are negatively charged as expected. The bridging hydrogen atoms are charged more negatively than the terminal hydrogens: H^b -0.45, H^t -0.33 in In$_2$H$_6$; H^b -0.43, H^t -0.32 in Tl$_2$H$_6$.

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