

# Low Valencies and Periodic Trends in Heavy Element Chemistry. A Theoretical Study of Relativistic Effects and Electron Correlation Effects in Group 13 and Period 6 Hydrides and Halides

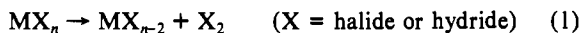
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**Abstract:** A wide range of compounds has been investigated theoretically by extensive ab initio computations in order to study the vertical and horizontal periodic trends in element–ligand bond stabilities and the occurrence of low valencies in the chemistry of heavy elements. We have studied the following: (1) group 13 hydrides and fluorides, MX and MX<sub>3</sub> (M = B, Al, Ga, In, Tl; X = H, F); (2) various hydrides and fluorides of the 6th period, viz., AuH, HgH<sub>2</sub>, TlX, TlX<sub>3</sub> (D<sub>3h</sub>), PbX<sub>2</sub> (C<sub>2v</sub>), PbX<sub>4</sub> (T<sub>d</sub>), BiX (C<sub>∞v</sub>; <sup>3</sup>Σ<sup>-</sup>), BiX<sub>3</sub> (C<sub>3v</sub>), and BiX<sub>5</sub> (D<sub>3h</sub> and C<sub>4v</sub>) (X = H, F); (3) the thallium compounds TlX and TlX<sub>3</sub> (X = H, F, Cl, Br, I). At the best level of treatment of electron correlation (quadratic configuration interaction), the calculated molecular properties are in good agreement with the available experimental results. From the ab initio calculated values of dissociation energies, D<sub>e</sub>, of MX<sub>n</sub>, we have derived the internal energies of X<sub>2</sub> elimination, of disproportionation of MX<sub>n-2</sub>, and of X<sub>2</sub> exchange between different elements in the gas phase. Our conclusions are summarized here. (1) Low valencies in compounds of the heavy elements arise naturally as a consequence of the periodic trend toward lower M–X bond strength with increasing atomic number, in agreement with an earlier analysis of experimental thermochemical data by Drago. Relativistic effects in the 6th period significantly augment this trend, but are not dominant. (2) Within the group 13 compounds MX<sub>3</sub>, elimination of X<sub>2</sub> is strongly endoergic but is less so for the heavier elements M. For TlX<sub>3</sub>, ΔU<sub>0</sub> for X<sub>2</sub> elimination varies in the order X = F > Cl > Br > I > H, despite a diminishing relativistic reduction of ΔU<sub>0</sub> along this series. (3) In the series TlX<sub>3</sub>, PbX<sub>4</sub>, BiX<sub>5</sub>, the tendency to eliminate X<sub>2</sub> and achieve a lower coordination number increases sharply between lead and bismuth, i.e., Bi<sup>IV</sup> is a markedly stronger oxidant than Pb<sup>IV</sup>. Relativistic contributions are almost constant along the series, though they clearly assist the oxidizing ability of these elements in their highest valency. (4) For the 6th period MX<sub>n-2</sub> compounds, the fluorides all strongly resist disproportionation, whereas disproportionation of monomeric TlH and PbH<sub>2</sub> is favored and is assisted by relativity. For the univalent group 13 hydrides and for BF, disproportionation is decisively assisted by the formation of M<sub>2</sub> from atomic M. (5) Thallium(III)–X bonds are weaker than thallium(I)–X bonds by ca. 30% except in the case of X = H. The strong binding between highly electronegative fluorine and thallium(I) favors the formation of 3TlF and TlX<sub>3</sub> from TlF<sub>3</sub> and 3TlX (X = Cl, Br, I, H). (6) Mulliken population analysis reveals no discernible trend in *ns* population between AlX<sub>3</sub> and TlX<sub>3</sub> (X = H, F) and thus provides no computational evidence for an especially inert 6s pair. (7) Although relativistic contributions play an important role in the chemistry of the 6th period elements, there is no evidence that the 6s electrons are more inert than the s electrons of lighter elements. Thus, there is no special “inert pair effect” for the 6th period elements, and it is inappropriate to use this term to designate the low valencies of heavier elements.

## I. Introduction

The aim of this work is to gain insight into the tendency to low valency in the chemistry of heavy elements by studying theoretically, at both nonrelativistic and relativistic levels, the change in internal energy, ΔU<sub>0</sub>, of the decomposition reaction shown in eq 1.



It is well known that the post-lanthanide elements thallium, lead, and bismuth form compounds (notably, halides and oxides) in which the elements are uni-, di- and trivalent, respectively, i.e., two below the characteristic group valency.<sup>1-3</sup> Sidgwick termed this behavior the *inert pair effect*<sup>1</sup> and attributed it to the corelike nature of the 6s electrons. The remarkable physical properties and the low reactivity of elemental mercury have also been attributed to the inertness of the 6s<sup>2</sup> electron pair. Although the phenomenon of lower valency is most evident for these heavy elements, similar behavior does appear elsewhere in the periodic table. For example, compounds of divalent tin and germanium (e.g., SnCl<sub>2</sub> and GeCl<sub>2</sub>) are well established, and elements that follow the filling of the first and second transition series are noticeably less stable in their highest oxidation states than are their lighter congeners.

Many textbooks<sup>3</sup> note that the term “inert pair effect” is merely a label rather than an explanation of the phenomenon. Drago<sup>4</sup>

has analyzed the hypothesis of an inert pair effect for the chlorides of groups 13 and 14, pointing out that inertness of the 6s electrons should be reflected in markedly larger 6s ionization potentials (IP). As shown in Figure 1, there is a slight increase in IP from the 5th to the 6th period of the periodic table. Drago noted, however, that the 4s electrons are stabilized even more than the 6s electrons, even though elements such as germanium and gallium do not show an inert pair effect to the same extent as lead and thallium. From careful analysis of the standard heats of the gas-phase decomposition reaction 1, where M is any group 13 or 14 element and X is chloride, Drago concluded that with increasing atomic number the bond energy decreases as a consequence of a decrease in the covalent contribution to the M–Cl bond for compounds of the heavier elements. Within the hybridization model, it may be argued that, for the heavier elements, the bond energies of the

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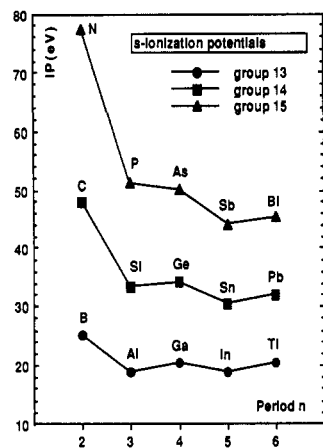
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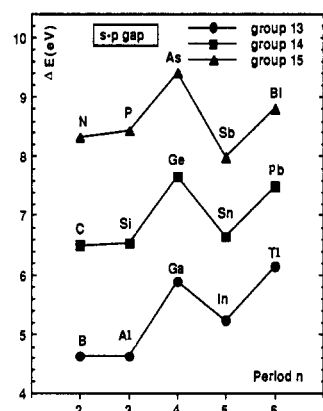
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**Figure 1.** Experimental  $ns^2(^1S_0) \rightarrow ns^1(^2S_{1/2})$  ionization potentials, IP (ref 5), for the group 13 ( $B^+$  to  $Tl^+$ ), group 14 ( $C^{2+}$  to  $Pb^{2+}$ ), and group 15 ( $N^{3+}$  to  $Bi^{3+}$ ) elements ( $n = 2-6$ ). The trend in the second s ionization potentials  $ns^2(^2S_{1/2}) \rightarrow ns^0(^1S_0)$  is very similar to the trend shown in this graph.



**Figure 2.** Experimental  $ns^2(^1S_0) \rightarrow ns^1np^1(^3P_0)$  excitation energies  $\Delta E$  (ref 5) for the group 13 ( $B^+$  to  $Tl^+$ ), group 14 ( $C^{2+}$  to  $Pb^{2+}$ ), and group 15 ( $N^{3+}$  to  $Bi^{3+}$ ) elements ( $n = 2-6$ ).

higher halides are insufficient to balance the energy required for s-p hybridization. Although the s-p separations (Figure 2)<sup>5</sup> show a more marked increase from the 5th to the 6th period than do the ionization potentials (Figure 1), the variation in bond stabilities of the group 13 and 14 compounds discussed above is still unexplained. The graphs shown in Figures 1 and 2 have already been discussed by Nyholm.<sup>6</sup> The "zigzag" behavior of physical and chemical properties down a group in the periodic table has long been recognized<sup>7</sup> and has been discussed on the basis of variations of electronegativity.<sup>3,8</sup>

Attempts have been made to ascribe both the zigzag behavior<sup>10</sup> and the presumed inertness of the 6s electrons<sup>10,11</sup> to relativistic effects. A rough explanation of the underlying phenomenon is that the relativistic mass-velocity operator acts on the inner tail of the 6s orbital, causing an overall contraction of the 6s density.<sup>12</sup>

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**Table I.** Nonrelativistic Hartree-Fock (HF), Relativistic Dirac-Fock (DF), and Experimental Ionization Potentials (IP)  $6s^2(^1S_0) \rightarrow 6s^1(^2S_{1/2})$  and Excitation Energies ( $\Delta E$ )  $6s^2(^1S_0) \rightarrow 6s^16p^1(^3P_0)$  for Hg,  $Tl^+$ ,  $Pb^{2+}$ , and  $Bi^{3+}$  (in eV)

	HF <sup>a</sup>	DF <sup>b</sup>	exp <sup>c</sup>	$\Delta_R$ <sup>d</sup>	$\Delta_{cor}$ <sup>e</sup>
	IP $6s^2(^1S_0) \rightarrow 6s^1(^2S_{1/2})$				
Hg	6.830	8.533	10.43	-1.703	-1.90
$Tl^+$	15.709	18.399	20.42	-2.690	-2.02
$Pb^{2+}$	26.102	29.819	31.93	-3.717	-2.11
$Bi^{3+}$	37.781	42.607	45.3 <sup>f</sup>	-4.826	-2.7 <sup>f</sup>
	$\Delta E$ $6s^2(^1S_0) \rightarrow 6s^16p^1(^3P_0)$				
Hg	2.145	3.199	4.667	-1.054	-1.468
$Tl^+$	3.416	4.772	6.131	-1.356	-1.359
$Pb^{2+}$	4.587	6.271	7.486	-1.684	-1.215
$Bi^{3+}$	5.702	7.414	8.798	-1.712	-1.384

<sup>a</sup> Calculated by means of program MCHF (ref 15). <sup>b</sup> Including QED

effects; calculated by means of program MCFD (ref 16). <sup>c</sup> From ref 5.

<sup>d</sup> Relativistic effects  $\Delta_R(IP) = IP_{NR} - IP_R$  and  $\Delta_R(\Delta E) = \Delta E_{NR} - \Delta E_R$ .

<sup>e</sup> Correlation effects  $\Delta_{cor}IP = IP_R - IP_{exp}$  and  $\Delta_{cor}(\Delta E) = \Delta E_R - \Delta E_{exp}$ .

<sup>f</sup> The trend in  $\Delta_{cor}IP$  suggests that the experimental value for the ionization potential  $6s^2(^1S_0) \rightarrow 6s^1(^2S_{1/2})$  of  $Bi^{3+}$  may be overestimated.

This effect reaches a maximum for group 11 elements such as gold,<sup>13</sup> but is still very large for the elements thallium, lead, or bismuth. The increase in both s ionization potential and the s-p energy gap from the 5th to the 6th period (as shown in Figures 1 and 2) is indeed a relativistic effect. Comparison of the theoretical and experimental 6s ionization potentials and 6s  $\rightarrow$  6p excitation energies given in Table I shows clearly that this effect can become more important than electron correlation in the valence region. This relativistic effect on the 6s pair has been invoked by several authors to rationalize low valency (in most cases without quantitative computational justification) and has been equated to Sidgwick's inert pair effect (see, for example, discussions in refs 13 and 14).

The phenomenon of lower valencies depends on both the heavy element (M) and the choice of ligand, e.g., thallium(III) halides tend to be unstable with respect to thallium(I) halides, whereas  $Tl(CH_3)_3$  is a stable compound at room temperature and  $TlCH_3$  is unknown.<sup>17</sup> Thus, even if relativistic effects are responsible for the emergence of lower valencies,<sup>11</sup> the strong dependence on ligand has to be explained. As a class, the alkyls are closely related to the hydrides, and the stability of group 13 hydrides  $MH_3$  is a matter of considerable interest. Despite early claims,<sup>18</sup> it seems unlikely that  $InH_3$  and  $TlH_3$  are sufficiently stable to be isolated.<sup>19</sup> Only  $BH_3$ ,<sup>20</sup>  $B_2H_6$ ,<sup>21</sup> and, recently,  $Ga_2H_6$ <sup>22</sup> have been studied to

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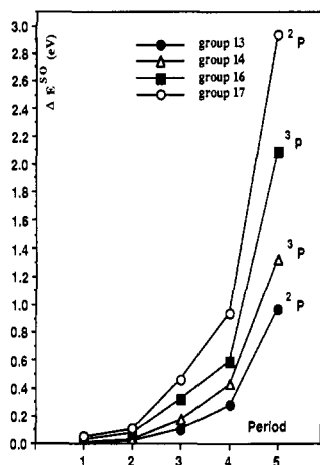
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**Figure 3.** Experimental fine structure splitting  $\Delta E^{\text{SO}}$  in electronvolts for the ground states of the group 13 (B–Tl;  $^2P_{1/2}/^2P_{3/2}$ ), group 14 (C–Pb;  $^3P_0/^3P_2$ ), group 16 (O–Po;  $^3P_2/^3P_0$ ), and group 17 (F–At;  $^2P_{3/2}/^2P_{1/2}$ ) elements. The experimental values are from ref 5. The  $^2P_{1/2}/^2P_{3/2}$  splitting for At was calculated by means of the numerical Dirac–Fock program MCDP/BENA by Grant and co-workers (ref 16). In the case of Te and Po the  $^3P_2/^3P_1$  splitting was used.

any extent by spectroscopic methods. GaH<sub>3</sub> and InH<sub>3</sub> have been observed by mass spectroscopy, and estimates of bond stabilities have been made.<sup>23</sup> Liang et al.<sup>24</sup> predicted the vibrational spectra of B<sub>2</sub>H<sub>6</sub>, Al<sub>2</sub>H<sub>6</sub>, and Ga<sub>2</sub>H<sub>6</sub> and suggested that Al<sub>2</sub>H<sub>6</sub> may be stable in the gas phase. In general, however, with the exception of boron hydrides,<sup>25</sup> there are few theoretical investigations on group 13 MH<sub>3</sub> compounds or their dimers M<sub>2</sub>H<sub>6</sub>.<sup>21,26–31</sup> For purposes of comparison, therefore, it is important to establish accurate theoretical bond stabilities of group 13 hydrides, as undertaken here.

In this paper, we explore theoretically the descriptive chemistry of a full vertical period (boron to thallium, hydrides and fluorides), of successive 6th row elements (gold through thallium to bismuth, hydrides and fluorides), and of the ligand sequence X = H, F, Cl, Br, I in TlX and TlX<sub>3</sub>. The methods, basis sets, and pseudopotentials we used are described in section II. The results are presented and discussed in section III, and our conclusions are summarized in section IV.

## II. Methods

Relativistic (R) and nonrelativistic (NR) Hartree–Fock (HF) calculations, including electron correlation by quadratic configuration interaction (QCI) and Møller–Plesset (MP<sub>n</sub>,  $n = 2-4$ ) on a series of group 13 hydrides and fluorides (MX and MX<sub>3</sub>; M = B, Al, Ga, In, Tl; X = H, F), on various hydrides and fluorides of the 6th period elements (AuH, HgH<sub>2</sub>, PbX<sub>2</sub> (C<sub>2v</sub>), PbX<sub>4</sub> (T<sub>d</sub>), BiX (C<sub>∞v</sub>;  $^3\Sigma^-$ ), BiX<sub>3</sub> (C<sub>3v</sub>), and BiX<sub>5</sub> (D<sub>3h</sub> and C<sub>4v</sub>) (X = H, F), and on the other thallium halides (TlX and TlX<sub>3</sub>; X = Cl, Br, I) and their dissociation products (H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>), have

been carried out. For TlI<sub>3</sub> the two possible structures, (i) trigonal planar and (ii) bent with a linear I<sub>3</sub><sup>-</sup> unit, are compared at the Hartree–Fock level (HF) of theory (NRHF and RHF). Dipole moments for the diatomics are given at the configuration interaction level (with single and double substitutions only, CISD, computed at the QCI(T) geometries). The comparative performance of these methods applied to the compounds will be compared in detail elsewhere.<sup>32</sup>

For heavy elements of groups 13, 14, 16, and 17, atomic relativistic fine structure effects must be allowed for; they will be referred to as spin–orbit coupling (SO) in the following discussion, because this is usually the main contributor. Figure 3 demonstrates the importance of SO coupling in heavy elements. The dissociation energies,  $D_e$ , of all compounds are therefore corrected for this effect. We also investigated the effect of spin–orbit coupling at the molecular level for the representative diatomics TlBr and TlI. Modified versions of the the program packages GAUSSIAN86/88,<sup>33</sup> TURBOMOLE,<sup>34</sup> and UHREL<sup>35</sup> were used for all calculations. The nonrelativistic and spin–orbit averaged relativistic pseudopotentials for In, Au, Hg, Tl, Pb, and Bi were taken from refs 28 and 36–40. The spin–orbit coupled model Hamiltonian for Tl, Br, and I was chosen as given in refs 28 and 37. The basis sets used are as follows (some of the d exponents are taken from Huzinaga et al.,<sup>41</sup> the numbers given in brackets for B, Al, and Ga follow the basis set notation by Poirier et al.<sup>42</sup>).

(i) **All-Electron.** For H a contracted Huzinaga (9s)/[6s] basis set<sup>43</sup> with p polarization functions given by Lie and Clementi<sup>44</sup> and a diffuse s function with exponent 0.01; for F a 6-311+G\* basis set;<sup>33</sup> for Ga a contracted Dunning (15s/11p/6d)/[11s/8p/4d] basis set (31.3.1)<sup>42</sup> (using the exponent 0.207 for the additional d function); for B a Lie and Clementi<sup>44</sup> basis set (5.57.2) with addition of a diffuse p function with exponent 0.015 and a d polarization function with exponent 0.4; for Al a McLean and Chandler<sup>45</sup> basis set (13.13.1) plus a diffuse p function with exponent 0.015 and a d polarization function with exponent 0.21.

(ii) **Pseudopotential.** NR and R basis sets for Br and I are listed in refs 38 and 39; NR and R basis sets for Tl are given in ref 28; for Bi an NR and R (7s/6p/1d) basis set<sup>39</sup> with d exponent 0.17; for Cl a Durand (4s/4p) basis set<sup>46</sup> extended by (2s/1p/1d) with exponents (0.06; 0.02/0.0495/0.56); the Pb basis sets are given in ref 38; for Au the basis set described in ref 36 was used; for Hg the basis set is given in ref 39;

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for In we used a (4s/4p) Durand basis set<sup>46</sup> and added a set of (2s/2p/1d) functions with exponents (0.03; 0.01/0.45; 0.015/0.16).

For some of the atoms treated as all-electron or pseudopotential systems, we kept the core orbitals inactive in the electron correlation procedures as follows (frozen core definitions are given in square brackets): [1s] for B and F; [1s2s2p] for Al; [1s2s2p3s3p3d] for Ga; [5s5p] for Au and Hg. The orbital space in the other atoms and the valence orbital space defined in the pseudopotential procedure were kept fully active. For the relativistic and nonrelativistic pseudopotentials for Tl, Pb, and Bi the [Pt] core definition was used, whereas for Au and Hg we chose the more accurate (but CPU expensive) [Kr4d<sup>10</sup>4f<sup>14</sup>] core. The reason is simply that a [Pt] core definition for gold<sup>32</sup> and mercury would lead to large errors in metal–ligand core–core repulsion and core-polarization effects, as discussed in detail by Stoll et al.<sup>47</sup> For Tl, Pb, and Bi, such corrections are small, and these elements can be treated as 6s6p valence electron systems.<sup>28,38</sup> The dissociation energies and reaction energies are not corrected for zero-point vibrational contributions (ZPVC). In the discussion that follows, relativistic effects in a molecular or atomic property  $P$  are defined as  $\Delta_R P = P_{NR} - P_R$ .

### III. Results and Discussion

**Molecular Properties.** The results of our molecular calculations are listed in Tables II–V, and these will be discussed in turn below. In almost all cases the performance of the QCI method is excellent; bond distances, force constants, dipole moments, and most dissociation energies agree well with available experimental data.<sup>4,20,32,49,50</sup> For example, for BF<sub>3</sub> the estimated dissociation energy is 1923 ± 35 kJ/mol, which compares well with our QCI result of 1828 kJ/mol. We therefore conclude that the basis sets and correlation methods used in this work are sufficient to study the decomposition reaction 1. In contrast, for the halogens, X<sub>2</sub>, the calculated dissociation energies shown in Table II are much less than those obtained experimentally. Fortunately, for a given X this is a constant error in the calculation of  $\Delta U_0$  for decomposition reaction 1. Moreover,  $\Delta U_0$  values are not strongly dependent on the level of electron correlation in MX<sub>m</sub>,<sup>32</sup> and so this error seems to cancel out. For example,  $\Delta U_0(\text{TlF}_3 \rightarrow \text{TlF} + \text{F}_2)$  at the HF level is 424 kJ/mol, and this compares reasonably well with the more accurate QCI value of 441 kJ/mol (Table II). To achieve better agreement for the X<sub>2</sub> dissociation energies, it would be necessary to use very large basis sets. Further, one would also have to take into account spin–orbit coupling at the molecular level for the heavier halides Br and I<sup>37</sup> and include high-level configuration interactions, as has been done for a series of diatomic bromine-containing compounds with a modified G1 theory.<sup>51</sup> Such lengthy procedures were not appropriate here, given the large number of compounds studied.

Relativistic effects in several compounds of the 6th period elements have already been analyzed.<sup>13,17,28,32,36–38,52</sup> The change in dissociation energy due to the action of the SO operator must comprise an atomic spin–orbit part and a molecular spin–orbit part:

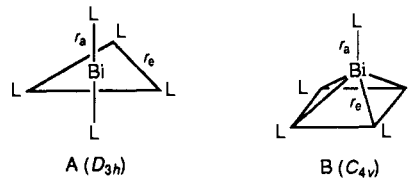
$$\Delta_{\text{SO}} D_e = \Delta_{\text{SO}}^A D_e + \Delta_{\text{SO}}^M D_e \quad (2)$$

For most molecules in their electronic ground states, it is generally assumed that the molecular contribution can be neglected as a consequence of p<sub>1/2</sub>/p<sub>3/2</sub> mixing at the equilibrium geometry to give almost pure  $\sigma$ -bonding.<sup>52</sup> Theoretical calculations on thallium and lead hydrides show that molecular SO contributions are small, e.g., for TlH<sub>3</sub>  $|\Delta_{\text{SO}}^M D_e|$  is less than 1% of  $|\Delta_{\text{SO}}^A D_e|$  at the HF level.<sup>28</sup> It is also found that  $|\Delta_{\text{SO}}^M D_e(\text{TlH}_3)|$  is less than  $|\Delta_{\text{SO}}^M D_e(\text{TlH})|$ .<sup>28</sup> As a test, we studied SO coupling at the HF level in the diatomic

molecules TlBr and TlI in more detail with the use of spin–orbit coupled pseudopotentials,<sup>28,35,37</sup> since both the ligand and the metal atom show large SO splittings at the atomic level.<sup>5</sup> SO effects decrease the thallium–ligand bond distance by only 0.004 Å in TlH,<sup>28</sup> by 0.039 Å in TlBr, and by 0.043 Å in TlI, so that the total relativistic bond contractions at the HF level are 0.033 Å for TlH, 0.029 Å for TlBr, and 0.046 Å for TlI. Incidentally, the excellent agreement between the SO-corrected QCI bond distance of 2.819 Å in TlI and the experimental value of 2.814 Å<sup>49</sup> indicates the quality of the pseudopotentials we used. The molecular SO contribution increases the dissociation energy by 8.8 kJ/mol in TlBr and by only 0.1 kJ/mol in TlI. These are relatively small amounts compared with the atomic contributions,  $\Delta_{\text{SO}}^A D_e$ , which are 76.8 kJ/mol for TlBr and 92.4 kJ/mol for TlI<sup>5</sup> and are not expected to change significantly in a CI calculation. Thus, molecular SO contributions improve our calculated dissociation energies only slightly; they certainly do not change the trends discussed in this work. In calculating reaction energies for the decomposition reaction 1, therefore, SO coupling effects can reasonably be neglected at the present level.

The sequence in  $\Delta_R D_e$  for different oxidation states of a given 6th row metal,  $\Delta_R D_e(\text{MX}_n) > \Delta_R D_e(\text{MX}_{n-2}) > \Delta_R D_e(\text{MX}_{n-4})$ , correlates with decreasing 6s participation in M–X bonding in the same sequence (cf. Table III). This is indicated by the progressive localization of 6s electrons, as measured by  $n_s$  (cf. Table III). For example, the relativistic reduction of  $D_e$  (QCI values) decreases in the sequence BiH<sub>5</sub> (180 kJ/mol) > BiH<sub>3</sub> (43 kJ/mol) > BiH (11 kJ/mol), while  $n_s$  grows from 1.3 through 1.7 to 1.9.<sup>53</sup>

For the species BiX<sub>5</sub> (X = H, F) and for TlI<sub>3</sub>, additional structures of different point group symmetries were calculated, because the ground-state geometry was not obvious. For example, PPh<sub>5</sub>, AsPh<sub>5</sub>, Sb(4-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>, and Bi(4-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>(2-FC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> are trigonal bipyramidal ( $D_{3h}$ , A) in the solid state, whereas SbPh<sub>5</sub> and BiPh<sub>5</sub> are square pyramidal ( $C_{4v}$ , B).<sup>54</sup> Several group 15



compounds MX<sub>5</sub> (X = H, F) have been investigated theoretically;<sup>55,56</sup> the calculated  $C_{4v}$  structures are all transition states within the Berry pseudorotation from one  $D_{3h}$  form into another.<sup>56</sup> A vibrational analysis of BiH<sub>5</sub> in the  $C_{4v}$  arrangement revealed one imaginary frequency of B<sub>1</sub> symmetry corresponding to the  $\delta_a$  normal mode.<sup>57</sup> The activation energy  $\Delta E_a$  for the  $D_{3h} \rightarrow C_{4v}$  transition is very small, generally ca. 10 kJ/mol. This is also the case for BiH<sub>5</sub> and BiF<sub>5</sub> (bottom of Table II). Relativistic and correlation effects change  $\Delta E_a$  only slightly. Hence, the structural differences in the crystalline pentaaryl compounds can reasonably be attributed to intermolecular forces.

Solid TlI<sub>3</sub> does not have the expected trigonal planar ( $D_{3h}$ ) arrangement with Tl<sup>III</sup> (C), but has the bent Tl<sup>I</sup> structure D with a linear I<sub>3</sub><sup>-</sup> unit (C<sub>s</sub>).<sup>58</sup> We find by calculation that structure

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**Table II.** Molecular Properties of Group 13 Hydrides and Fluorides, Thallium Halides, Gold and Mercury Hydrides, and Lead and Bismuth Hydrides and Fluorides<sup>a</sup>

	$r_c$		$D_e$		$\Delta U_0$	
	MP2	QC1	MP2	QC1	MP2	QC1
Group 13 Hydrides						
BH	1.230	1.241	326.7	340.9	112.9	116.5
BH <sub>3</sub>	1.188	1.193	1127.0	1133.0	372.6	343.3
AlH	1.665	1.674	276.4	292.5	62.6	68.1
AlH <sub>3</sub>	1.586	1.593	820.4	844.5	116.3	103.2
GaH	1.675	1.696	253.2	272.8	39.4	48.4
GaH <sub>3</sub>	1.577	1.586	759.7	788.8	78.8	67.2
InH	1.838	1.850	224.4	242.4	10.6	18.0
InH <sub>3</sub>	1.725	1.734	670.1	701.8	18.0	10.6
TlH	1.899 (1.924)	1.912 (1.934)	165.5 (241.7)	184.7 (259.1)	-48.4 (27.9)	-39.7 (34.7)
TlH <sub>3</sub>	1.745 (1.831)	1.756 (1.839)	544.8 (674.0)	584.0 (729.5)	-48.4 (4.6)	-49.5 (21.6)
Group 13 Fluorides						
BF	1.273	1.278	740.9	709.9	686.8	672.7
BF <sub>3</sub>	1.317	1.316	1932.6	1827.7	1083.5	1043.3
AlF	1.723	1.722	637.2	607.0	583.1	569.8
AlF <sub>3</sub>	1.678	1.676	1638.8	1546.3	893.4	864.8
GaF	1.813	1.813	559.2	539.1	505.1	501.9
GaF <sub>3</sub>	1.745	1.744	1356.4	1281.5	689.0	667.9
InF	1.999	1.997	518.4	490.7	464.3	453.5
InF <sub>3</sub>	1.923	1.923	1217.4	1129.0	590.8	563.8
Thallium Halides						
TlF	2.060 (2.061)	2.060 (2.061)	448.4 (536.1)	424.6 (511.4)	394.3 (482.0)	387.4 (474.2)
TlF <sub>3</sub>	1.958 (2.002)	1.958 (1.998)	1021.1 (1327.1)	939.9 (1237.3)	464.5 (679.6)	440.8 (648.2)
TlCl	2.480 (2.524)	2.484 (2.479)	360.4 (396.1)	345.3 (422.7)	264.2 (299.9)	253.7 (331.1)
TlCl <sub>3</sub>	2.314 (2.357)	2.319 (2.364)	809.9 (1065.5)	756.8 (1004.7)	257.0 (440.0)	228.3 (391.8)
TlBr	2.629 (2.627)	2.633 (2.631)	308.3 (401.3)	295.5 (386.5)	234.3 (308.8)	224.8 (297.8)
TlBr <sub>3</sub>	2.468 (2.520)	2.478 (2.527)	665.9 (960.1)	626.2 (907.0)	209.6 (373.7)	189.3 (343.1)
TlI	2.859 (2.871)	2.862 (2.876)	243.8 (350.7)	233.1 (334.5)	199.6 (269.4)	191.3 (256.6)
TlI <sub>3</sub>	2.686 (2.744)	2.699 (2.756)	490.9 (803.4)	457.0 (757.0)	158.7 (290.0)	140.2 (266.6)
Gold, Mercury, Lead, and Bismuth Compounds						
AuH	1.499 (1.732)	1.522 (1.770)	275.6 (178.7)	285.7 (197.5)	123.5 (-70.3)	122.6 (-53.8)
HgH <sub>2</sub>	1.629 (1.761)	1.652 (1.786)	300.5 (346.2)	332.5 (373.3)	-127.2 (-81.5)	-116.3 (-75.5)
PbH <sub>2</sub>	1.849 (1.857)	1.866 (1.868)	338.3 (481.8)	376.3 (515.8)	-89.4 (54.1)	-72.5 (67.0)
PbH <sub>4</sub>	1.755 (1.805)	1.767 (1.813)	766.4 (1025.5)	824.1 (1073.8)	0.4 (116.0)	-1.0 (109.2)
PbF <sub>2</sub>	2.047 (2.014)		822.9 (1005.4)		714.7 (897.2)	
PbF <sub>4</sub>	1.972 (1.966)		1336.7 (1828.1)		401.2 (711.3)	
BiH	1.819 (1.837)	1.837 (1.851)	192.0 (203.6)	213.2 (224.4)	-21.9 (-10.3)	-11.2 (0.0)
BiH <sub>3</sub>	1.809 (1.827)	1.826 (1.839)	649.7 (696.2)	705.9 (748.6)	222.0 (268.5)	257.1 (299.8)
BiH <sub>5</sub>	1.892 (1.895)	1.907 (1.906)	723.0 (917.7)	819.1 (999.4)	-354.4 (-206.2)	-335.6 (-198.0)
BiF	2.080 (2.070)	2.084 (2.072)	345.0 (366.8)	322.5 (345.3)	290.0 (312.7)	285.3 (308.1)
BiF <sub>3</sub>	2.038 (2.025)		1140.1 (1225.8)		1031.9 (1117.6)	
BiF <sub>5</sub>	2.022 (2.007)		1432.7 (1777.3)		184.4 (440.1)	
Dissociation Products						
H <sub>2</sub>	0.736	0.742	427.7	448.8		
F <sub>2</sub>	1.425	1.453	108.2	74.5		
Cl <sub>2</sub>	2.024	2.046	192.5	183.2		
Br <sub>2</sub>	2.310 (2.294)	2.335 (2.318)	148.0 (185.1)	141.4 (177.4)		
I <sub>2</sub>	2.724 (2.707)	2.754 (2.734)	88.4 (162.7)	83.7 (155.9)		

<sup>a</sup> Element-ligand M-X bond distances,  $r_c$ , in Å, atomization energies  $D_e(\text{MX}_n \rightarrow \text{M} + n\text{X})$  in kJ (mol  $\text{MX}_n$ )<sup>-1</sup>, and reaction energies  $\Delta U_0(\text{MX}_n \rightarrow \text{MX}_{n-2} + \text{X}_2)$  for diatomics:  $\text{MX} \rightarrow \text{M} + 1/2\text{X}_2$  in kJ mol, using the calculated dissociation energies for the diatomics  $\text{X}_2$  listed at the bottom of this table. All relativistic values for  $D_e$  are corrected for atomic spin-orbit coupling  $\Delta E_{\text{SO}}$  obtained from ref 5 (in kJ/mol): B 0.1, Al 0.9, Ga 6.6, In 17.6, Tl 62.1, Pb 102.0, Bi 0.0, F 1.6, Cl 3.5, Br 14.7, I 30.3. For the heavy elements Au, Hg, Tl, and Pb, the nonrelativistic values are given in brackets. Zero-point vibration contributions (ZPVC) are not included, i.e.,  $D_e^0 = D_e - \text{ZPVC}$  ( $D_e^0 < D_e$ ). For additional structural properties, see ref 32. The difference in total energy between the more stable trigonal planar Tl(III) structure and the bent Tl(I) structure ( $r_c(\text{Tl(I)}) = 3.904$  Å (RHF);  $r_c(\text{Tl(I)}) = 4.319$  Å (NRHF)) containing a linear I<sub>3</sub> unit at the HF level is  $\Delta E = 127.9$  kJ/mol (R) and 289.1 kJ/mol (NR). Activation energy ( $\Delta E_a$ ) for Berry pseudorotation ( $(D_{3h}) \rightarrow (C_{4v}) \rightarrow (D_{3h})$ ) in kJ/mol: BiH<sub>5</sub> 13.4 (R), 12.7 (NR); BiF<sub>5</sub> 7.4 (R), 8.0 (NR). The calculated angles are as follows (in degrees): TlI<sub>3</sub> ( $C_{\infty v}$ ) 88.4 (RHF), 105.8 (NRHF); PbH<sub>2</sub> 90.5 (RQCI), 91.7 (NRQCI); PbF<sub>2</sub> 96.7 (RMP2), 95.4 (NRMP2); BiH<sub>3</sub> 90.7 (RQCI), 91.9 (NRQCI); BiF<sub>3</sub> 96.4 (RMP2), 94.4 (NRMP2). For other data, see ref 32.

C is the minimum (gas phase) arrangement. Structure D has a large permanent dipole moment ( $\mu = 5.90$  D at the RHF level) in contrast to C ( $\mu = 0$  D), which would cause strong electrostatic interactions between individual TlI<sub>3</sub> (C<sub>v</sub>) units; this may explain why an ionic lattice is preferred in the solid state. Moreover, the population analysis of D (Table III) shows large charge separations between the Tl atom and the I<sub>3</sub> unit, suggestive of large ionic character in the Tl-I bond. This gives rise to a shallow potential surface and a Tl-I-I bond angle  $\alpha$  of about 90°. Relativistic

effects are very important in determining the energy difference between the two possible structures of TlI<sub>3</sub>: in the nonrelativistic case, structure C lies ca. 290 kJ/mol below structure D, compared to ca. 130 kJ/mol below D in the relativistic case. This suggests that the preference of solid TlI<sub>3</sub> for structure D over C is a lattice effect that is assisted by relativistic contributions.



C (trigonal planar)

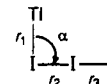
D (bent with linear I<sub>3</sub><sup>-</sup> unit)

Table III. Hartree-Fock Mulliken Orbital Populations,  $n_s$  and  $n_p$ , and Gross Metal Charges,  $q$ , for Hydrides and Fluorides of Group 13, for Halides of Thallium(I) ( $MX_{n-2}$ ) and Thallium(III) ( $MX_n$ ), and for  $PbX_2/PbX_4$ ,  $BiX_3/BiX_5$ , and  $BiX$  ( $X = H, F$ )<sup>a</sup>

M/X	$MX_{n-2}$			$MX_n$		
	$n_s$	$n_p$	$q$	$n_s$	$n_p$	$q$
B/H	1.85	1.04	0.08	0.98	1.76	0.20
Al/H	1.79	0.76	0.39	0.78	1.09	0.97
Ga/H	1.83	0.77	0.37	0.86	1.25	0.81
In/H	1.83	0.68	0.47	0.82	0.97	1.18
Tl/H	1.86 (1.80)	0.72 (0.72)	0.43 (0.45)	0.98 (0.75)	0.99 (0.99)	1.05 (1.25)
B/F	2.02	0.91	-0.05	0.69	1.56	0.30
Al/F	1.95	0.47	0.47	0.49	0.71	1.34
Ga/F	2.02	0.42	0.49	0.59	0.83	1.33
In/F	1.97	0.34	0.66	0.52	0.58	1.81
Tl/F	1.99 (1.95)	0.26 (0.31)	0.75 (0.72)	0.54 (0.38)	0.45 (0.46)	2.03 (2.10)
Tl/Cl	2.00 (2.00)	0.39 (0.45)	0.58 (0.50)	0.96 (0.73)	0.90 (0.95)	1.06 (1.14)
Tl/Br	1.96 (1.98)	0.47 (0.42)	0.51 (0.57)	0.99 (0.77)	0.83 (0.95)	1.08 (1.11)
Tl/I	1.98 (1.95)	0.46 (0.52)	0.52 (0.48)	1.16 (0.91)	1.07 (1.11)	0.67 (0.82)
$TlI_3 (C_3)$				1.99 (1.93)	0.45 (0.50)	0.55 (0.50)
Pb/H	1.71 (1.63)	1.45 (1.48)	0.83 (0.85)	0.97 (0.85)	1.47 (1.39)	1.59 (1.75)
Pb/F	2.13 (2.00)	0.67 (0.77)	1.14 (1.13)	0.97 (0.69)	1.07 (1.05)	1.87 (2.04)
Bi/H	1.67 (1.54)	2.20 (2.29)	1.19 (1.30)	1.30 (1.10)	1.80 (1.66)	2.17 (2.46)
$(C_{4v})$				1.30 (1.10)	2.01 (1.71)	2.09 (2.39)
BiH	1.91 (1.87)	2.74 (2.75)	0.36 (0.39)			
Bi/F	2.07 (2.03)	1.11 (1.18)	1.80 (1.74)	1.06 (0.81)	1.51 (1.45)	2.48 (2.72)
$(C_{4v})$				1.03 (0.76)	1.71 (1.53)	2.43 (2.66)
BiF	2.03 (2.01)	2.34 (2.37)	0.61 (0.59)			

<sup>a</sup> Nonrelativistic values are in brackets. For group 13 compounds,  $n_s + n_p + n_d + q = 3$ ; the d contributions are important for several compounds and can be obtained from the  $n_s$ ,  $n_p$ , and  $q$  values listed in this table. For the diatomic compounds, CISD or MP2 populations have been obtained which are only slightly different from the HF values (see ref 32).

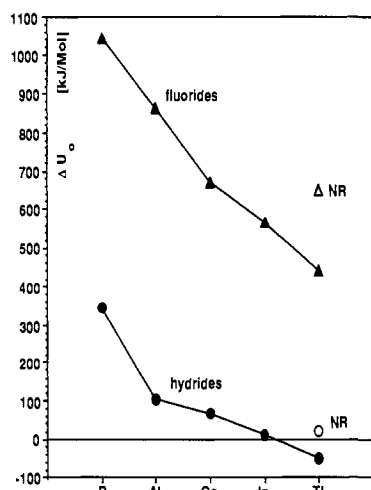


Figure 4. Calculated QCI reaction energies (at 0 K) in kilojoules/mole for the reaction  $MX_3 \rightarrow MX + X_2$  ( $M = B, Al, Ga, In, Tl; X = H, F$ ). Zero-point vibrational contributions are not included.

**Group 13 Hydrides and Halides.** The change in internal energy  $\Delta U_0$  of reaction 1 for the group 13 hydrides and fluorides is shown in Figure 4. Although zigzag trends similar to those shown in Figure 1 may characterize properties such as electronegativity or chemical reactivity,<sup>8</sup> they are not evident in the calculated energetics of the molecules studied here. Specifically, there is no sudden decrease between indium and thallium of the stability of the oxidation state +3 relative to +1. The decreasing stability of the higher oxidation state is rather due to a monotonic downward trend in the  $\Delta U_0$  values (eq 1) for the group 13 hydrides and fluorides; the only relatively large change in  $\Delta U_0$  occurs from  $BH_3$  to  $AlH_3$ , as pointed out and analyzed in more detail by Kutzelnigg.<sup>59</sup> Although relativistic effects contribute substantially to the decrease of  $\Delta U_0$  in the decomposition of  $TlH_3$  and  $TlF_3$ , they are not the main reason for the low valency observed for most inorganic thallium compounds.

The reductive elimination reaction (eq 1) forms one X-X bond at the expense of two M-X bonds. For a given metal, the bond

energies are substantially the same in  $MX_3$  and  $MX$  (generally within 5% for the hydrides and within 20% for the fluorides). So it is the general tendency to weaker M-X bonding in the heavier elements (regardless of oxidation state) that determines the trends in Figure 4 (see also ref 59 for a detailed discussion). Considered in detail, the ratio of  $M^{III}-X$  to  $M^I-X$  bond energies ( $= \frac{1}{3}D_e(MX_3)/D_e(MX)$ ) for the hydrides takes values 1.11 (B), 0.96 (Al), 0.96 (Ga), 0.97 (In), and 1.05 (Tl), and this variation obviously cannot account for the relative instability of  $TlH_3$ . For the fluorides, the corresponding values are 0.85 (B), 0.85 (Al), 0.79 (Ga), 0.77 (In), and 0.74 (Tl), and this diminishing  $M^{III}/M^I$  bond energy ratio contributes (though not decisively) to the decreasing stability of the trivalent fluorides from boron to thallium. The discontinuity in the values of the ratio for the hydrides arises from complexities in the relativistic contribution to atomization processes, specifically to the formation of atomic M, which do not influence  $\Delta U_0$  (eq 1). Note that the SO coupling of the metal M ( $\Delta E_{SO}$ ) contributes proportionately more to atomization of  $MX$  than to  $MX_3$ . In consequence, the ratio of  $MX_3$  to  $MX$  bond energies is unsuitable as a general index of valency trends.

The s populations exhibit a marked zigzag variation from boron to thallium (Table III), and the s populations in  $BH_3$  and  $TlH_3$  are almost identical; similarly, there is no discernible trend in  $n_s$  between  $AlF_3$  and  $TlF_3$ . We conclude that, at least for the compounds studied here, there is no special 6s inert pair effect. In short, the  $ns^2$  pair is not especially inert for heavy element hydrides and fluorides. The low valency in the heavy element compounds arises naturally as a periodic trend towards weaker bonding, which cannot be explained either in terms of trends in atomic s ionization potentials or by s-p separations, but may be attributed to a decrease in the metal-ligand covalent bond character, as suggested by Drago.<sup>4</sup> The population analyses (Table III) and both calculated and experimental dipole moments (Figure 5) of the diatomic group 13 hydrides and fluorides show that ionicity increases from boron to thallium, consistent with Drago's explanation.<sup>4</sup>

The experimental values of  $\Delta U_0$  for the group 13 chlorides are smaller than those for the fluorides, but follow the same trend. Accordingly, we have extended our calculations to the heavier halides of thallium(III). The results for the entire  $TlX_3$  family are displayed in Figure 6. The computed order of stability of the thallium(III) compounds, with respect to eq 1, is  $TlF_3 > TlCl_3 > TlBr_3 > TlI_3 > TlH_3$ . This is in accordance with their known chemistry, e.g., solid  $TlI_3$  exists only as the thallium(I) compound  $Tl^+I_3^-$  and even  $TlCl_3$  is a powerful oxidant.<sup>60</sup> The relativistic

(59) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 272; *Angew. Chem.* 1984, 96, 262.

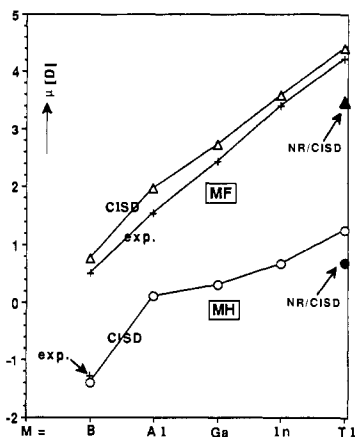


Figure 5. CISD dipole moments ( $\mu$ ) for the diatomic group 13 fluorides and hydrides. Experimental values are from ref 50.

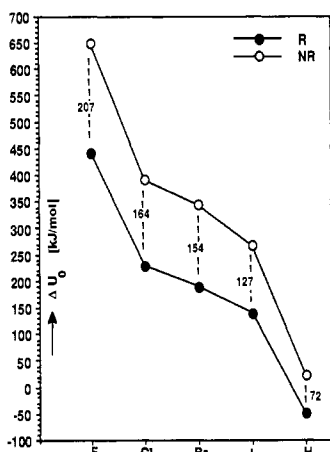


Figure 6. Calculated nonrelativistic and relativistic QCI internal energy changes  $\Delta U_0$  (at 0 K) in kilojoules/mole for the reaction  $TlX_3 \rightarrow TlX + X_2$  ( $X = F, Cl, Br, I, H$ ). The numbers on the graph represent the relativistic changes in  $\Delta U_0$  for each ligand  $X$ . Zero-point vibrational contributions are not included.

contribution favors the elimination of  $X_2$  and formation of  $TlX$  (eq 1) but *decreases* in the sequence  $X = F$  to  $X = I$  (and  $H$ ). This is reflected in reduced participation of the  $6s$  pair in bonding with decreasing electronegativity of the halide. Thus,  $n(6s)$  (Table III) ranges from 0.54 in  $TlF_3$  to 1.16 in  $TlI_3$  ( $D_{3h}$ ). Relativity serves to shift the plot in Figure 6 to lower  $\Delta U_0$  values but actually flattens the general trend. The thallium(I) halides are therefore favored by both the relativistic destabilization of  $Tl^{III}$  and the natural downward trend in stability from the fluoride to the hydride at the nonrelativistic level. It is, however, this latter effect that dictates the trend within the set of halides. For a given halide, we expect the value of  $\Delta U_0$  to decrease from  $BX_3$  to  $TlX_3$ , as found computationally for  $MF_3$  (Figure 4). The stability trends for the halides and hydrides of group 14 (carbon to lead) and group 15 (phosphorus to bismuth) are likely to resemble those of group 13 depicted in Figure 4. We also predict that  $PbI_4$  ( $T_d$ ) and  $TlI_3$  ( $D_{3h}$ ) are thermodynamically stable in the gas phase with respect to the metal and  $I_2$ , contrary to an earlier suggestion.<sup>61</sup>

Solid-state effects may also contribute substantially to the stabilization of low valencies in heavy elements.<sup>4</sup> The large dipole moments of the diatomic thallium halides (between 4.40 D for  $TlF$  and 4.88 D for  $TlI$  at the relativistic CISD level) can be expected to give rise to rather large lattice energies and hence to high sublimation enthalpies  $\Delta H_s$  for the crystalline compounds. The few available measurements<sup>62</sup> indicate that the values of  $\Delta H_s$

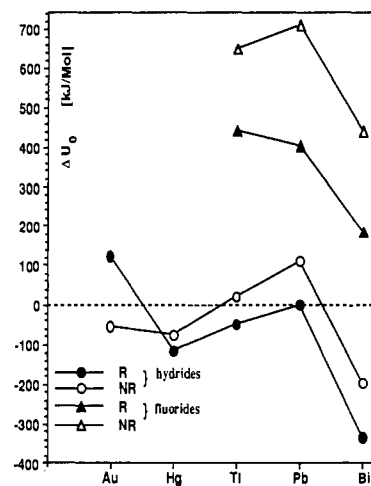


Figure 7. Calculated nonrelativistic and relativistic QCI reaction energies (at 0 K) in kilojoules/mole for the reaction  $MX_n \rightarrow MX_{n-2} + X_2$  ( $M = Au, Hg, Tl, Pb, Bi$ ). For the Au atom, the dissociation  $2AuH \rightarrow 2Au + H_2$  is used. MP2 values are used for  $PbF_4$  and  $BiF_5$ . Zero-point vibrational contributions are not included.

for the group 13 diatomics  $MX$  are 4–5 times larger than those of the  $MX_3$  compounds, the latter usually being between 15 and 30 kJ/mol. This results in a downward shift of the halide  $\Delta U_0$  curves along the series boron to thallium of about 40–120 kJ/mol, but it should not change the overall trend. Since  $PbF_2$  and  $BiF_3$  also have large dipole moments (at the RMP2 level:  $PbF_2 = 5.52$  D,  $BiF_3 = 6.09$  D), we can expect a similar shift for the groups 14 and 15 halides. Thus, relativistic effects influence lattice energies as well, as is clear from a comparison of the nonrelativistic and relativistic dipole moments (at the NRMP2 level;  $PbF_2 = 4.19$  D,  $BiF_3 = 5.23$  D). Such effects have not been considered in the past and certainly deserve detailed investigation.

Association may also occur in the gas phase:



The dimerization reaction 3 for the group 13 hydrides  $B_2H_6$ ,  $Al_2H_6$ , and  $Ga_2H_6$  has been considered theoretically by a number of authors.<sup>24,25,27,31</sup> The results obtained so far reveal that the dimerization is exothermic (disregarding entropy effects), but decreasingly so from boron to gallium. The dimerization of  $InH_3$  and  $TlH_3$  has also been discussed in some detail. Although processes 3 and 4 will shift the  $\Delta U_0$  plot in Figure 4 up or down, respectively, they are unlikely to change the general trend (at least not for the values published for the  $MH_3$  dimerization). However, such reactions are relevant to the question of the existence of the as yet unknown compounds  $InH_3$ ,  $In_2H_6$ ,  $TlH_3$ , and  $Tl_2H_6$ . The trends shown in Figure 4 suggest that the monomeric form of  $TlH_3$  is thermodynamically unstable in the gas phase.<sup>63</sup>

**Comparison of Stability of Compounds in the Series Au, Hg, Tl, Pb, and Bi.** Are relativistic effects the fundamental or dom-

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(63) The results obtained for the other group 13 hydrides (refs 24, 25, 27, 29, and 30) suggest that the dimerization energy for  $InH_3$  and  $TlH_3$  is above  $-90$  kJ/mol, i.e., if the dimerization energy from boron to thallium decreased linearly, the value might even be about  $-30$  kJ/mol. On the other hand, MP2 calculations on  $Tl_2H_2$  (ref 30) gave a dimerization energy of about  $-85$  kJ/mol. Consideration of reactions 3 and 4 therefore suggests that  $Tl_2H_6$  is thermodynamically unstable with respect to the decomposition  $Tl_2H_6 \rightarrow Tl_2H_2 + 2H_2$ . However,  $Tl_2H_6$  might be kinetically stable and perhaps could be studied in matrix isolation. We have therefore studied the transition state of the  $H_2$  abstraction at the HF level. This reaction may represent the crucial step in the decomposition of  $Tl_2H_6$  since it is exothermic at the relativistic level. However, preliminary calculations suggest that the  $H_2$  abstraction of  $TlH_3$  does not follow the symmetric  $C_{2v}$  pathway as indicated, but rather an asymmetric reaction path involving several possible channels for the  $H_2$  abstraction.

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Table IV. Computed Internal Energies for Some Disproportionation Reactions of Compounds  $\text{MX}_{n-2}$ , Containing 6th Period Elements in Low Valencies<sup>a</sup>

$\text{MX}_{n-2}$	$\Delta U(\text{R})$ - (disprop) <sup>b</sup>	$\Delta_{\text{R}}\Delta U$ - (disprop) <sup>c</sup>	disproportionation reaction
TlH <sup>d</sup>	-29.9	77.7	
TlF	334.0	-33.8	
TlCl	279.1	-8.7	$3\text{TlX} \rightarrow \text{TlX}_3 + 2\text{Tl}$
TlBr	260.3	-7.8	
TlI	242.4	4.4	
PbH <sub>2</sub>	-81.1	29.3	
PbF <sub>2</sub>	313.5	-127.6	$2\text{PbX}_2 \rightarrow \text{PbX}_4 + \text{Pb}$
BiH <sub>3</sub>	379.5	-106.1	
BiF <sub>3</sub>	502.5	-191.8	$2\text{BiX}_3 \rightarrow \text{BiX}_5 + \text{BiX}$
BiH	-66.3	-9.1	
BiF	-105.1	-20.3	$3\text{BiX} \rightarrow \text{BiX}_3 + 2\text{Bi}$

<sup>a</sup> Calculations are based on Table II and refer to gaseous monomers.

<sup>b</sup> Negative value of  $\Delta U$  implies that disproportionation is favored;  $\Delta U$  values refer to disproportionation of  $3\text{TlX}$ ,  $2\text{PbX}_2$ ,  $2\text{BiX}_3$ , or  $3\text{BiX}$ .

<sup>c</sup>  $\Delta_{\text{R}}\Delta U = \Delta U(\text{NR}) - \Delta U(\text{R})$ . <sup>d</sup> See also ref 48.

inant cause of the preference for low valency in heavy element compounds? Relativistic effects should decrease along the hydrides of Au, Hg, Tl, Pb, and Bi.<sup>11,13</sup> Relativistic effects stabilize the Au-H bond by  $-88.2$  kJ/mol but destabilize the Bi-H bond in  $\text{BiH}_3$  by  $+36.1$  kJ/mol (note that the relativistic contribution between gold and mercury changes sign). Figure 7 shows that except for AuH, relativistic effects decrease the stability of compounds in the high oxidation state but do *not* alter the underlying trend (there is also a relativistic decrease in the stability of AuF, in contrast to the behavior of AuH, which is explained elsewhere<sup>36</sup>). A particularly large *nonrelativistic* decrease in  $\Delta U_0$  occurs between  $\text{PbX}_4$  and  $\text{BiX}_5$  for  $\text{X} = \text{H}$  and  $\text{F}$ , which causes  $\text{Bi}^{\text{V}}$  to be a stronger oxidant than  $\text{Pb}^{\text{IV}}$ . Relativistic effects in the elimination of  $\text{F}_2$  from  $\text{BiF}_5$  account for ca. 260 kJ/mol (and 310 kJ/mol for  $\text{PbF}_4$ ). Clearly, in the absence of relativistic effects,  $\text{BiF}_5$  (and  $\text{PbF}_4$ ) would not be such a strong fluorinating agent. It is clear from Figure 7 that  $\text{BiH}_5$  is thermodynamically highly unstable and, not surprisingly, this molecule is unknown; however, organobismuth(V) compounds have been isolated.<sup>54,64</sup> Recent calculations have shown that the decomposition energies of  $\text{Hg}(\text{CH}_3)_2$ <sup>65</sup> and  $\text{Tl}(\text{CH}_3)_3$ <sup>17</sup> are similar to those of the corresponding hydrides. This result can be expected to be general and suggests that penta-aryl bismuth compounds  $\text{BiAr}_5$ <sup>54,66</sup> are also thermodynamically unstable; their stability at ambient temperature is likely to be kinetic. Lead and thallium in their higher oxidation states form many stable alkyls and aryls,  $\text{PbR}_4$ <sup>67</sup> and  $\text{TlR}_3$ .<sup>67</sup> In contrast to bismuth, corresponding compounds containing the elements in their lower oxidation states,  $\text{PbR}_2$  and  $\text{TlR}$ , are known only for  $\eta^5$ -cyclopentadienyl and related ligands and, in the case of lead, for the sterically bulky ligands  $\text{CH}(\text{SiMe}_3)_2$ <sup>68</sup> and  $2,4,6\text{-C}_6\text{H}_2(\text{CF}_3)_3$ .<sup>69</sup> Electronegative organic ligands that resemble fluoride more than hydride might serve to stabilize  $\text{Pb}^{\text{II}}$  and  $\text{Tl}^{\text{I}}$  with respect to  $\text{Pb}^{\text{IV}}$  and  $\text{Tl}^{\text{III}}$ . It should be mentioned that electron correlation effects make some contribution to the relatively large negative value of  $\Delta U_0$  for  $\text{HgX}_2$ ,<sup>32,70</sup> whereas they only play a minor role in the decomposition of  $\text{TlX}_2$ ,  $\text{PbX}_4$ , and  $\text{BiX}_5$  ( $\text{X} = \text{H}, \text{F}$ ).

It may be useful to compare the internal energies of successive  $\text{X}_2$  elimination reactions in the 6th row elements, that is, to compare decomposition reactions of  $\text{MX}_n$  (eq 1) and  $\text{MX}_{n-2}$  (eq

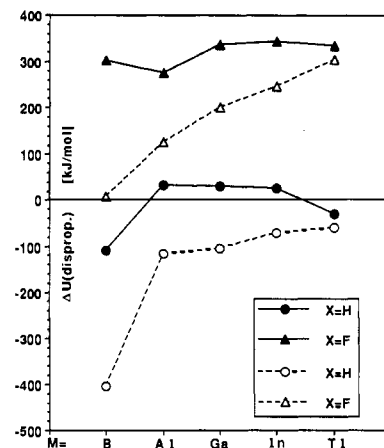
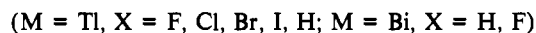
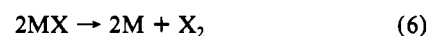


Figure 8. Disproportionation energies  $\Delta U(\text{disprop}) = 2\Delta U_0(\text{MX}) - \Delta U_0(\text{MX}_3)$  in kilojoules/mole for the group 13 ( $\text{M} = \text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Tl}$ ) hydrides and fluorides ( $\text{X} = \text{H}, \text{F}$ ). Values are taken from Table II. —,  $\Delta U(\text{disprop})$ ; ---,  $\Delta U(\text{disprop}) - \Delta E(\text{M}_2)$ .

5 or 6) in order to assess the relative stability of the intermediate oxidation state:



For this purpose, we consider only gas-phase reactions of the monomers. Reactions 1, 5, and 6 have in common the cleavage of two M-X bonds and the formation of one molecule of  $\text{X}_2$ . The differences in  $\Delta U_0$  for these reactions correspond to the internal energies of disproportionation of the intermediate oxidation state  $n$  to the  $n + 2$  oxidation state and the metallic element (or to  $\text{Bi}^{\text{I}}$  in the case of  $\text{BiX}_3$ ), and will be referred to as  $\Delta U(\text{disprop})$ . Table IV summarizes these disproportionation energies for intermediate oxidation state compounds of the 6th period. In the sequence  $\text{Tl}^{\text{I}}$ ,  $\text{Pb}^{\text{II}}$ , and  $\text{Bi}^{\text{III}}$ , the fluorides (especially  $\text{BiF}_3$ ) are strongly resistant to disproportionation. The hydride  $\text{BiH}_3$  is also predicted to be stable; indeed,  $[\text{BiH}_3]^+$  has been observed by mass spectroscopy.<sup>71</sup> In contrast,  $\text{TlH}$  and  $\text{PbH}_2$  are prone to disproportionation, as is in fact observed in the case of the corresponding alkyls and aryls. The relativistic contribution is significant in these cases and decisive for  $\text{TlH}$ , but is unimportant for the halides. Compared to  $\text{TlH}$ ,  $\text{BiX}$  disproportionates very readily to  $\text{Bi}^{\text{0}}$  and  $\text{Bi}^{\text{III}}$  in the case of both hydride and fluoride but *not* through relativistic effects, which actually favor  $\text{Bi}^{\text{I}}$ .

**Disproportionation of Univalent Group 13 Compounds.** Figure 8 displays the difference in  $\Delta U_0$  for the successive  $\text{X}_2$  elimination reactions for group 13 hydrides and fluorides. This is equivalent to consideration of the gas-phase disproportionation reaction, where all species are explicitly monomeric:



The internal energy of disproportionation  $\Delta U(\text{disprop})$  is defined:

$$\Delta U(\text{disprop}) = 2\Delta U_0(\text{MX}) - \Delta U_0(\text{MX}_3) = 3D_e(\text{MX}) - D_e(\text{MX}_3) \quad (8)$$

Figure 8 suggests that disproportionation according to eq 7 is accessible for the hydrides but strongly unfavorable for the fluorides. If some account is taken of the effect of aggregation of the free element by inclusion of the internal energy of dimerization of the group 13 element (eq 9), the tendency to disproportionation is now much increased for the lighter elements.



With this adjustment, the appropriate trend revealed in Figure 8 (dashed lines) is consistent with empirical inorganic chemistry, viz., univalency in group 13 is most favored for the heavier element

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Table V. Computed Internal Energies  $\Delta U_0$  for Inner-Sphere Redox (Halogen Transfer) Reactions of Compounds of Group 13 Elements

(a) $BX + MX_3 \rightarrow BX_3 + MX$						
M =	B	Al	Ga	In	Tl	
$\Delta U_0(X = H)$	0	-240	-276	-333	-393	(-322) <sup>a</sup>
$\Delta U_0(X = F)$	0	-179	-375	-480	-603	(-392) <sup>a</sup>

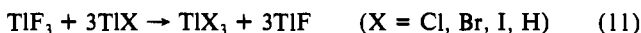
  

(b) $TlF_3 + 3TlX \rightarrow TlX_3 + 3TlF$						
X =	F	Cl	Br	I	H	
$\Delta U_0(R)$	0	-55	-74	-92	-364	
$\Delta U_0(NR)$	0	-30	-48	-54	-252	

<sup>a</sup>Numbers in parentheses are nonrelativistic values calculated on the assumption that  $\Delta U_0(R) \equiv \Delta U_0(NR)$  for  $BX_n$ .

fluorides and is intrinsically unstable for all hydrides. While this simple picture neglects many undoubtedly important factors, such as lattice energies, entropy effects, and kinetic stabilization, it nevertheless reveals  $\Delta U(\text{disprop})$  as a valuable index of the intrinsic bond enthalpy terms.

**Inner-Sphere Redox Reactions Involving Halide Transfer.** A worthwhile extension of the previous discussion is to construct balanced redox reactions which express the energetic differences between individual systems and which embody the periodic trends already discussed. Of the many possibilities, we have chosen to illustrate those in eqs 10 and 11, for which  $\Delta U_0$  values are presented in Table V. This strategy has two advantages. First,  $BX + MX_3 \rightarrow BX_3 + MX$  (M = Al, Ga, In, Tl; X = H, F) (10)



various extraneous effects, such as the energy of formation of  $X_2$ , spin-orbit coupling, entropy, and lattice energy, are minimized or eliminated. Second, the symmetry of these *isodesmic* reactions should cause the trends in  $\Delta U_0$  values to reflect more closely those in  $\Delta G$ . Equation 10 expresses the oxidizing power of  $MX_3$  relative to  $BX_3$ , which increases down the group for both hydrides and fluorides. This trend arises from the preference for formation of three B-X bonds and one M-X bond, M being the heavier element. Relativity clearly contributes to the oxidizing ability of thallium(III) relative to indium(III) (cf. Table V), as it does also for bismuth(V) vs antimony(V) and lead(IV) vs tin(IV).

Equation 11 expresses the oxidizing power of  $TlF_3$  relative to the heavier halides and hydride of thallium(III). It may at first sight seem surprising that, for example,  $TlI_3$  is more readily formed in this reaction than is  $TlCl_3$  when the former is the less stable according to  $\Delta U_0$  for reaction 1 or the  $D_e$  values (Table II). Since  $M^I-X$  bonds are about 30% stronger than the corresponding  $M^{III}-X$  bonds and fluoride forms the strongest M-X bonds, the overriding tendency is to form three  $M^I-F$  bonds rather than three  $M^{III}-F$  bonds. Relativity enhances this trend without basically altering it.

Finally, it is worth noting the opposite secondary effects of relativity on the chemistry of the heavy transition elements and the heavy main group elements. It is well established experimentally<sup>72</sup> and theoretically<sup>11,13</sup> that for the hexahalides  $[MX_6]^{z-}$  (M = Zr to Pd and Hf to Pt; X = F, Cl, Br; z = 0, 1, 2, 3) such effects cause systematic stabilization of the *higher* oxidation states for the 5d elements relative to their 4d congeners. This can be rationalized in terms of efficient screening of the valence d shell by the relativistically contracted inner s orbitals, which reduces d electron ionization energies in compounds of the third transition series.

#### IV. Summary and Conclusions

We draw the following conclusions from our calculations.

(1) In group 13, element-ligand bond strengths decrease monotonically with increasing atomic number, which ensures that

elimination of  $X_2$  (eq 1) is increasingly favored. For the fluorides, but not the hydrides, this tendency is enhanced by the weakness of the individual  $M^{III}-F$  bond relative to the  $M^I-F$  bond, the bond energy ratio varying from 85% to 75% down the group.

(2) Relativity assists in stabilizing thallium(I) relative to thallium(III), especially for the fluorides, but does not determine the trend outlined in 1.

(3) As judged by Mulliken population analysis, there is no discernible trend in outermost s population ( $n_s$ ) between  $AlX_3$  and  $TlX_3$  and thus no computational evidence for an especially inert 6s electron pair in the trivalent state. Naturally, the s population increases upon reduction, e.g., from  $Tl^{III}$  to  $Tl^I$ , thus increasing the inert pair character of the  $M^I$  compound, and this is reinforced by relativistic effects.

(4) It follows from 1 that, for the group 13 elements, there is a steady increase in the oxidizing ( $X_2$  transfer) ability with increasing atomic number of the  $MX_3$  compounds (X = H, F) considered as gas-phase monomers of  $D_{3h}$  symmetry. There is no abrupt change between  $InX_3$  and  $TlX_3$  caused by relativistic effects.

(5) For thallium trihalides and trihydrides, elimination of  $X_2$  is strongly endoergic but less disfavored for the heavier halides;  $\Delta U_0$  decreases in the order X = F > Cl > Br > I > H. In contrast, the relativistic contribution favors  $TlX$  but becomes smaller with decreasing electronegativity of the ligand from X = F to X = I and X = H (Figure 6).

(6) In the 6th period hydride series, there is a progressive increase in relativistic bond weakening from  $AuH$  to  $BiH_5$ , according to computed contributions to bond dissociation energy, bond length, and force constant. This increase is attributed to the dilution of 6s participation by a large 6p admixture in the metal-hydrogen bond. The average bond energies,  $D_e/n$ , corrected for atomic SO terms (QCI-computed and corrected), vary by no more than 10% from  $HgH_2$  to  $BiH_5$  ( $185 \pm 20$  kJ/mol) and from  $TlF_3$  to  $BiF_5$  ( $310 \pm 25$  kJ/mol). The relativistic contribution is always destabilizing for these compounds and numerically larger for fluoride than hydride. These effects are well illustrated in computed trends in  $\Delta U_0$  for  $MX_n$ , as well as in  $D_e$ .

(7) The stability of intermediate oxidation states can be assessed by examining the energetics of appropriate disproportionation reactions (Table IV). Within the 6th period  $MX_{n-2}$  compounds, the subvalent fluorides strongly resist disproportionation. In contrast, disproportionation of monomeric  $TlH$  and of  $PbH_2$  is energetically favorable, and this process is significantly assisted by relativity. For the hydrides of the group 13 elements and for  $BF$ , disproportionation is decisively assisted by aggregation of the free element; this has been computationally modeled by the formation of  $M_2$  from atomic M, a process which is strongly favored for the lighter elements.

(8) It is similarly informative to compile from the individual  $D_e$  data the internal energies for balanced, *isodesmic* redox reactions between compounds in various oxidation states, e.g.,  $BF + AlF_3 \rightarrow BF_3 + AlF$  and  $TlF_3 + 3TlH \rightarrow TlH_3 + 3TlF$ . This leads to conclusions that are not otherwise self-evident, e.g., the preference of the highly electronegative fluorine for thallium(I) over thallium(III) in halide exchange reactions between these oxidation states (Table V).

(9) In the series  $TlX_3$ ,  $PbX_4$ ,  $BiX_5$ , the tendency to eliminate  $X_2$  and reduce the coordination number increases sharply between lead and bismuth, even at the nonrelativistic level, i.e.,  $Bi^V$  is a markedly stronger oxidant than  $Pb^{IV}$ . Relativistic contributions are almost constant along the series (ca. 100 and 250 kJ/mol for X = H and F, respectively) and so do not alter the trend, but they clearly assist the oxidizing power of the elements in their highest oxidation states (Figure 7).

(10) The energetics of the alkyls and aryls of the 6th period elements are probably similar to those of the hydrides, so that the stability of compounds such as  $BiPh_5$ ,  $PbMe_4$ , and  $TlMe_3$  is likely to be kinetic.

(11) Lattice energy effects have not been included in our calculations, but are obviously important in the normal descriptive chemistry of the elements we have considered. Such effects may

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account for the existence of  $\text{III}_3$  as  $\text{TI}^+\text{I}_3^-$  in the solid state.

In summary, we have calculated a number of molecular properties, such as bond lengths, dipole moments, and dissociation energies, for a range of inorganic molecules, and where experimental data are available, the agreement is satisfactory. The most informative quantities for comparative purposes are the internal energies ( $\Delta U_0$ ) for eq 1. For the 6th period elements, we have identified the relativistic and nonrelativistic contributions to  $\Delta U_0$  and find that, although the former contribute as much as 25% to the reduction of  $\Delta U_0$ , they are not decisive in determining the trend along the period and are not associated with a particular corelike character of the 6s electrons. It is true that, in many of the compounds we have considered, the s electrons play only a small part in bonding and in that sense can be regarded as corelike, even for the lighter elements. Thus,  $\sigma$ -bonding involves mainly the valence p electrons, and the familiar concept of s-p hybridization is not relevant to the calculated electronic structures. The term inert pair effect has also been used in overlap and density arguments (see, for example, ref 73). As Drago<sup>4</sup> suggested, however, there is no special inert pair effect on valency for the 6th period elements; moreover, there is no particular relativistic contribution that determines preferred oxidation states. Finally, although the ab initio calculations satisfactorily reproduce the

trends in  $\Delta U_0$ , there remains the challenge of relating the resulting numerical data to an intuitively comprehensible bonding model within the framework of descriptive inorganic chemistry.

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**Registry No.** BH, 13766-26-2; BH<sub>3</sub>, 13283-31-3; AlH, 13967-22-1; AlH<sub>3</sub>, 7784-21-6; GaH, 13572-92-4; GaH<sub>3</sub>, 13572-93-5; InH, 13939-13-4; InH<sub>3</sub>, 15060-45-4; TIH, 13763-69-4; TIH<sub>3</sub>, 82391-14-8; BF, 13768-60-0; BF<sub>3</sub>, 7637-07-2; AlF, 13595-82-9; AlF<sub>3</sub>, 7784-18-1; GaF, 13966-78-4; GaF<sub>3</sub>, 7783-51-9; InF, 13966-95-5; InF<sub>3</sub>, 7783-52-0; TIF, 7789-27-7; TIF<sub>3</sub>, 7783-57-5; TlCl, 7791-12-0; TlCl<sub>3</sub>, 13453-32-2; TlBr, 7789-40-4; TlBr<sub>3</sub>, 13701-90-1; TII, 7790-30-9; TII<sub>3</sub>, 13453-37-7; AuH, 13464-75-0; HgH<sub>2</sub>, 72172-67-9; PbH<sub>2</sub>, 101764-35-6; PbH<sub>4</sub>, 15875-18-0; PbF<sub>2</sub>, 7783-46-2; PbF<sub>4</sub>, 7783-59-7; BiH, 17000-07-6; BiH<sub>3</sub>, 18288-22-7; BiH<sub>5</sub>, 124652-39-7; BiF, 13827-23-1; BiF<sub>3</sub>, 7787-61-3; BiF<sub>5</sub>, 7787-62-4.

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## Structures, Bonding, and Absorption Spectra of Amine-Sulfur Dioxide Charge-Transfer Complexes

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**Abstract:** The 1:1 and 2:1 charge-transfer (CT) molecular complexes between ammonia and the methyl-substituted amines,  $\text{CH}_3\text{NH}_2$  (MA),  $(\text{CH}_3)_2\text{NH}$  (DMA), and  $(\text{CH}_3)_3\text{NH}$  (TMA), and  $\text{SO}_2$  have been examined using ab initio molecular orbital theory. Equilibrium structures have been obtained at a variety of levels of theory including MP2/6-31G(d), and binding energies were determined at the MP3/6-31+G(2d,p) level. Correction for electron correlation is found to be necessary for an accurate description of the structures and stabilities of these amine- $\text{SO}_2$  complexes. For TMA- $\text{SO}_2$ , the calculated N-S equilibrium distance is reduced dramatically, by 0.18 Å, in going from the Hartree-Fock level to the MP2 level of theory. The calculated enthalpies of complex formation ( $\Delta H$ , 298 K) for  $\text{NH}_3\cdot\text{SO}_2$ , MA- $\text{SO}_2$ , DMA- $\text{SO}_2$ , and TMA- $\text{SO}_2$  are 4.5, 6.7, 7.9, and 10.7 kcal mol<sup>-1</sup>, respectively, and the corresponding N-S bond lengths are 2.79, 2.62, 2.46, and 2.36 Å, respectively. The computed formation enthalpy and geometry for TMA- $\text{SO}_2$  are in good accord with experimental data. The trends of geometry and stability of these amine- $\text{SO}_2$  complexes can be rationalized in terms of the donor strength of the amines (TMA > DMA > MA >  $\text{NH}_3$ ). The 2:1 adducts,  $(\text{NH}_3)_2\cdot\text{SO}_2$ , MA<sub>2</sub>· $\text{SO}_2$ , DMA<sub>2</sub>· $\text{SO}_2$ , and TMA<sub>2</sub>· $\text{SO}_2$ , are all predicted to be thermodynamically stable, with binding energies slightly less than the corresponding 1:1 complexes, and are predicted to be experimentally accessible species in the gas phase. The bonding characteristics of the amine- $\text{SO}_2$  CT complexes have been investigated by charge density analysis. The N-S bond is characterized by a strong ionic interaction. The charge-transfer component plays an important role in determining the stabilities of these donor-acceptor complexes. The calculated amount of charge transfer from the amine to  $\text{SO}_2$  are 0.04, 0.08, 0.13, and 0.18 eV for  $\text{NH}_3\cdot\text{SO}_2$ , MA- $\text{SO}_2$ , DMA- $\text{SO}_2$ , and TMA- $\text{SO}_2$ , respectively. The infrared and ultraviolet spectra of the 1:1 and 2:1 CT complexes were calculated for the first time. The computed vibrational frequencies and transition energies are consistent with experimental data.

### Introduction

Charge-transfer (or donor-acceptor) complexes are of importance in several phenomena of chemistry and biology.<sup>1</sup> The

trimethylamine-sulfur dioxide (TMA- $\text{SO}_2$ ) complex represents one of the best characterized charge-transfer complexes. The gas-phase and crystal structures have been determined by Fourier transform microwave spectroscopy<sup>2</sup> and X-ray crystallography,<sup>2,3</sup> respectively. The reaction thermodynamics have been studied in the gas phase as well as in solution by ultraviolet spectroscopy.<sup>4</sup>

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