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Equilibria in Free-Radical Chemistry: An Ab Initio Study of Hydrogen Atom Transfer Reactions between Silyl, Germyl, and Stannyl Radicals and Their Hydrides

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Ab initio calculations using a (valence) double-ζ pseudopotential (DZP) basis set, with (MP2, QCISD) and without (SCF) the inclusion of electron correlation, predict that the reactions of silyl, germyl, and stannyl radicals with silane, germane, stannane, trimethylsilane, trimethylgermane, and trimethylstannane proceed via transition states of C_{3v} or D_{3d} symmetry in which the attacking and leaving radical centers adopt a collinear arrangement. For reactions involving $^{\bullet}SiH_3$, $^{\bullet}GeH_3$ and $^{\bullet}SnH_3$, energy barriers of between 23.4 ($^{\bullet}SiH_3 + SnH_4$) and 86.0 ($^{\bullet}SnH_3 + SiH_4$) kJ$\cdot$mol^{-1} are predicted at the QCISD/DZP//MP2/DZP (+ ZPVE) level of theory. Specifically, the identity exchange reaction involving silane and the silyl radical is predicted to involve an energy barrier of some 53.6 kJ$\cdot$mol^{-1} at the highest level of theory, in good agreement with the available experimental data. The similar reactions involving germyl ($^{\bullet}GeH_3 + GeH_4$) and stannyl radicals ($^{\bullet}SnH_3 + SnH_4$) are predicted to have energy barriers of 47.0 and 38.9 kJ$\cdot$mol^{-1}, respectively, at the same level of theory. Inclusion of alkyl substitution on one of the heteroatoms in each reaction serves to alter the position of the hydrogen atom undergoing translocation in the transition state when compared with the unsubstituted series; the reactions of $H_3Y^{\bullet}$ with Me_3XH become "later" when compared with the analogous parent reaction ($H_3Y^{\bullet}$ with XH_4). Energy barriers of between 23.8 ($^{\bullet}SiH_3 + Me_3SnH$) and 98.3 ($^{\bullet}SnH_3 + Me_3SiH$) kJ$\cdot$mol^{-1} are predicted at the MP2/DZP (+ ZPVE) level of theory. The mechanistic implications of these computational data are discussed.

Introduction

Inter- and intramolecular homolytic addition chemistry occupies an important position in the chemical armory available to the synthetic chemist.[1] The formation of five- and six-membered rings through 5- and 6-*exo-trig* cyclizations of 5-hexenyl- and 6-heptenyl-type radicals[1,2] complements nicely the more traditional cycloaddition chemistry for the formation of rings and is often the method of choice for the preparation of rings in natural products synthesis.[1,2]

Invariably, free-radical syntheses involve chain processes, utilizing chain-carrying species such as tributylstannane,[3] tributylgermane,[4] and more recently, tris(trimethylsilyl)silane[5,6] together with precursors[7] designed to meet specific selectivity criteria.[1] The transformation of bromide **1** into $\Delta^{9(12)}$-capnellene (**2**) by the action of tributylstannane in a tandem (cascade) radical sequence (Scheme 1) demonstrates the power of the chemistry in question.[8] A knowledge of the rate constants (k_1, k_2, k_{Br}, k_H) associated with each of the reactions depicted in Scheme 1 allows, through control of reaction concentration, the required selectivity criteria to be met and the desired outome to be realized.[1]

Silyl, germyl, and stannyl radicals are very reactive species.[5,9] Reactions with oxygen, alkenes, alkynes, carbonyl compounds, and dichalcogenides and self-

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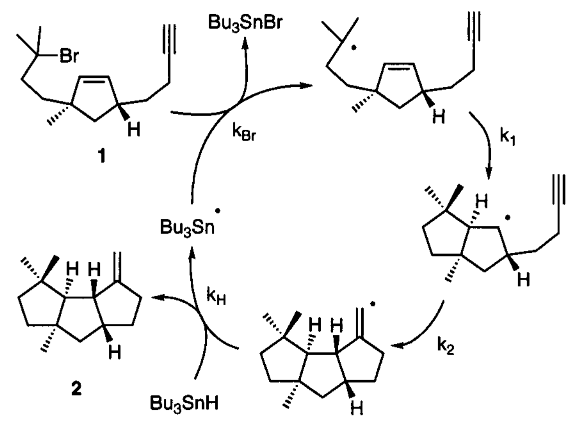
Scheme 1[a]



[a] Background: $Bu_3Sn^{\bullet} + Bu_3SnH \rightleftarrows Bu_3SnH + Bu_3Sn^{\bullet}$.

reaction are all potentially disruptive to the radical chain process depicted in Scheme 1.[9]

The identity reaction in which stannyl radical abstracts hydrogen from stannane (Scheme 1) is one competing reaction which might be expected to have little effect on the overall synthetic outcome during radical chain processes. Depending on the degree of predominance of these degenerate reactions, they can affect the efficiency of the overall radical chain by channelling stannyl radicals away from the required product-forming reactions. Degenerate background reactions have been reported by Crich and co-workers to lead to low conversion and prolonged reaction times when acyl radicals are generated from telluro esters.[10] Line broadening in NMR spectra of stannanes and exchange narrowing in ESR spectra of stannyl radicals has been attributed to a rapid exchange of hydrogen atoms between stannyl radicals and the corresponding stannane, and estimates in solution lead to energy barriers of less than about 8 $kJ\cdot mol^{-1}$ for these exchanges.[11] These degenerate processes cannot, therefore, be ignored during the design of synthetic procedures involving stannyl radicals.

In contrast, the gas-phase reaction of silyl radical ($SiH_3^{\bullet}$) with silane (SiH_4) is reported to have an energy barrier of more than 60 $kJ\cdot mol^{-1}$.[12] This value would preclude the degenerate exchange of hydrogen atoms between silicon centers from being important in radical reactions involving silanes; the activation energy for the abstraction of a hydrogen atom by a primary alkyl radical from triethylsilane is reported to be 33.5 $kJ\cdot mol^{-1}$.[5]

To provide further insight into potential background reactions of chain-carrying radicals, we now report the results of an extensive ab initio study of hydrogen-transfer reactions between silyl, germyl, and stannyl radicals with substituted and unsubstituted silanes, germanes, and stannanes. QCISD/DZP//MP2/DZP (+ ZPVE) calculations provide energy barriers of between 23.4 and 86.0 $kJ\cdot mol^{-1}$ for hydrogen atom exchange reactions involving silane, germane, and stannane, respectively.

Methods

Ab initio molecular orbital calculations were performed on a Sun SparcStation 5, Cray Y-MP4E/364, or Cray J916 computer using the Gaussian 92[13] or Gaussian 94[14] system of programs. Wherever possible, geometry optimizations were performed using standard gradient techniques at the SCF and MP2 levels of theory using a (valence) double-ζ pseudopotential basis set supplemented with polarization functions (DZP). Full details of this basis have been published elsewhere.[15–19] We demonstrated some time ago that this basis set outperforms many other pseudopotential bases as well as many double-ζ all-electron basis sets.[16] In previous work, results generated using DZP proved to be very similar to those obtained using 6-311G** for reactions involving chlorine and silicon.[17] All-electron techniques when applied to systems containing heavy elements can quickly become prohibitive in terms of computer resources;[16] the DZP basis set allows for quality computational data to be realized in systems containing elements such as germanium and tin.

All ground and transition states were verified by vibrational frequency analysis at the SCF level of theory. Except for structures involved in reactions of trisubstituted silanes, germanes, and stannanes, further single-point QCISD calculations and vibrational frequency analyses were performed on all MP2 optimized structures. Values of $\langle s^2 \rangle$ never exceeded 0.78 before annihilation of quartet contamination, indicating little spin contamination in all calculations. Zero-point vibrational energy corrections have been applied wherever possible; where these corrections are estimates based on a lower level of theory, these are indicated in parentheses.[20]

Results and Discussion

Reactions of Silyl, Germyl, and Stannyl Radicals with Silane, Germane, and Stannane. Searching of the H_7XY (X, Y = Si, Ge, Sn) potential energy surfaces at both the SCF/DZP and MP2/DZP levels of theory located structures **3**−**8** of D_{3d} or C_{3v} symmetry. These structures proved to be the transition states for the

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(20) "MP2/DZP + ZPVE" indicates that the zero-point correction is based on the MP2/DZP frequency calculation; "MP2/DZP (+ ZPVE)" or "QCISD/DZP//MP2/DZP (+ ZPVE)" indicates that the zero-point correction is an estimate based on the highest level frequency calculation performed on that system.

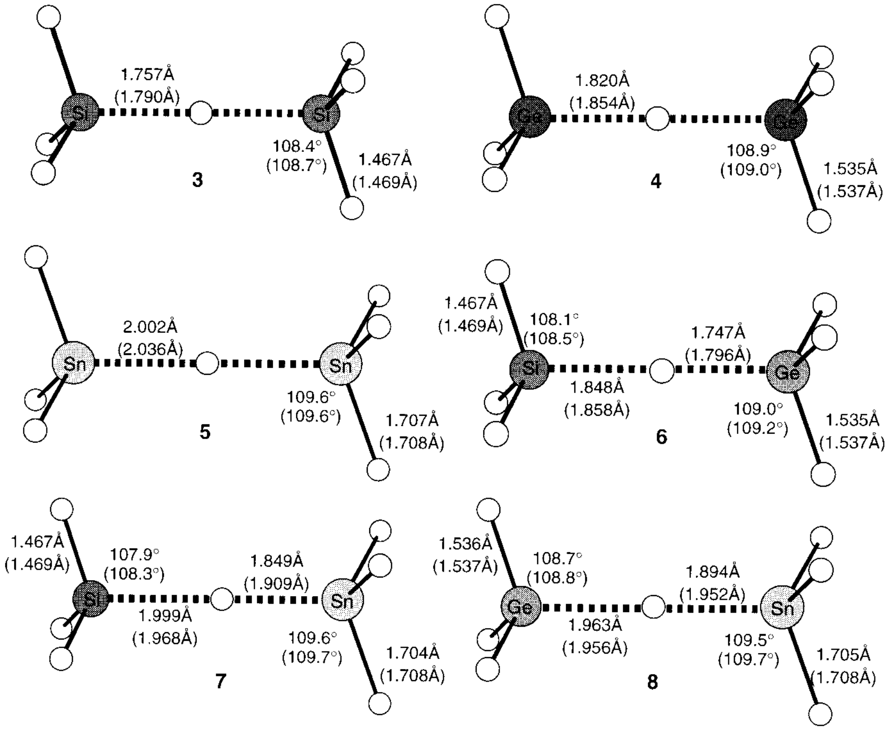

Figure 1.

transfer of hydrogen atoms between the various group(IV) centers upon frequency analysis and are displayed in Figure 1. Energies of all transition states located in this work are listed in Table 3; energies of the substituted and unsubstituted silanes, germanes, and stannanes and the corresponding radicals have been reported previously.[15,17−19]

Inspection of Figure 1 reveals $Si-H_{TS}$, $Ge-H_{TS}$, and $Sn-H_{TS}$ separations of 1.757, 1.820, and 2.002 Å in transition states **3**, **4**, and **5**, respectively, at the MP2/DZP level of theory; all transition-state distances are predicted to be slightly longer in the absence of electron correlation (1.790, 1.854, 2.036 Å).

It is well-established that the order of radical reactivity in homolytic substitution is $R_3Si^\bullet > R_3Ge^\bullet > R_3Sn^\bullet$.[21] With this in mind, the transition-state separations in structures **6**−**8** are not unexpected; the more reactive radical would be expected to be involved in the "earlier" transition state during attack at the hydride. For example, the $Si-H_{TS}$ separation in **6**, calculated to be 1.848 Å at the MP2/DZP level, is longer than the corresponding distance in **3**, while the $Ge-H_{TS}$ distance, at 1.747 Å at the same level, is somewhat shorter than the corresponding distance in structure **4**. This observation is consistent with silyl radical attack at germane involving an "earlier" transition state than that for the reaction of a germyl radical at silane. Similar trends are observed in the remaining "mixed" transition states (**7**, **8**).

Table 1. Calculated Energy Barriers[a] ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$) for the Hydrogen Atom Exchange Reactions between Silyl, Germyl, and Stannyl Radicals and Silane, Germane, and Stannane (Scheme 1, R = R′ = H) and the Transition-State (Imaginary) Frequencies (ν)[b]of Structures 3−8

X	Y	TS	method	$\Delta E_1^{\#}$	$\Delta E_1^{\#}$ + ZPVE[c]	$\Delta E_2^{\#}$	$\Delta E_1^{\#}$ + ZPVE[c]	ν
Si	Si	**3**	SCF/DZP	93.2	87.4	93.2	87.4	1800i
			MP2/DZP	65.7	58.2	65.7	58.2	1539i
			QCISD/DZP[d]	61.1	(53.6)	61.1	(53.6)	
Ge	Ge	**4**	SCF/DZP	80.7	73.1	80.7	73.1	1646i
			MP2/DZP	55.8	47.9	55.8	47.9	1421i
			QCISD/DZP[d]	54.9	(47.0)	54.9	(47.0)	
Sn	Sn	**5**	SCF/DZP	68.9	61.3	68.9	61.3	1462i
			MP2/DZP	48.6	40.6	48.6	40.6	1316i
			QCISD/DZP[d]	46.9	(38.9)	46.9	(38.9)	
Si	Ge	**6**	SCF/DZP	103.4	96.5	72.8	66.0	1683i
			MP2/DZP	78.3	69.5	46.6	39.6	1384i
			QCISD/DZP[d]	73.8	(65.0)	45.5	(38.5)	
Si	Sn	**7**	SCF/DZP	120.3	111.3	54.6	48.9	1446i
			MP2/DZP	102.4	91.2	31.2	24.9	985i
			QCISD/DZP[d]	97.2	(86.0)	29.7	(23.4)	
Ge	Sn	**8**	SCF/DZP	94.6	85.2	59.4	53.1	1488i
			MP2/DZP	75.5	65.5	35.9	29.1	1193i
			QCISD/DZP[d]	74.0	(64.0)	34.7	(27.9)	

[a] Energies in kJ·mol^{-1}. [b] Frequencies in cm^{-1}. [c] Values in parentheses are estimates based on MP2/DZP ZPVE corrections. [d] QCISD/DZP//MP2/DZP.

The trends established for the distances in structures **3**−**8** are reinforced by the calculated energy barriers for the respective hydrogen-transfer reactions (Table 1). For the identity exchange reactions involving silane, germane, and stannane, energy barriers ($\Delta E_1^{\#} = \Delta E_2^{\#}$) of 93.2, 80.7, and 68.9 kJ·mol^{-1} are calculated, respectively, at the SCF/DZP level. Inclusion of electron correlation (MP2) serves to lower these barriers to values of 65.7 (Si), 55.8 (Ge), and 48.6 (Sn) kJ·mol^{-1}, while at the QCISD level, values of 61.1, 54.9, and 46.9 kJ·mol^{-1} are calculated. The degree of convergence between MP2 and QCISD data provides confidence in the theoretical methods employed in this study. Zero-point vibrational energy (ZPVE) correction has the effect of further lowering the barriers by 7.5−8.0 kJ·mol^{-1}. MP2/DZP + ZPVE barriers of 58.2, 47.9, and 40.6 kJ·mol^{-1} are obtained for the silane, germane, and stannane reactions, respectively, while QCISD/DZP//MP2/DZP (+ ZPVE) calculations predict values of 53.6,

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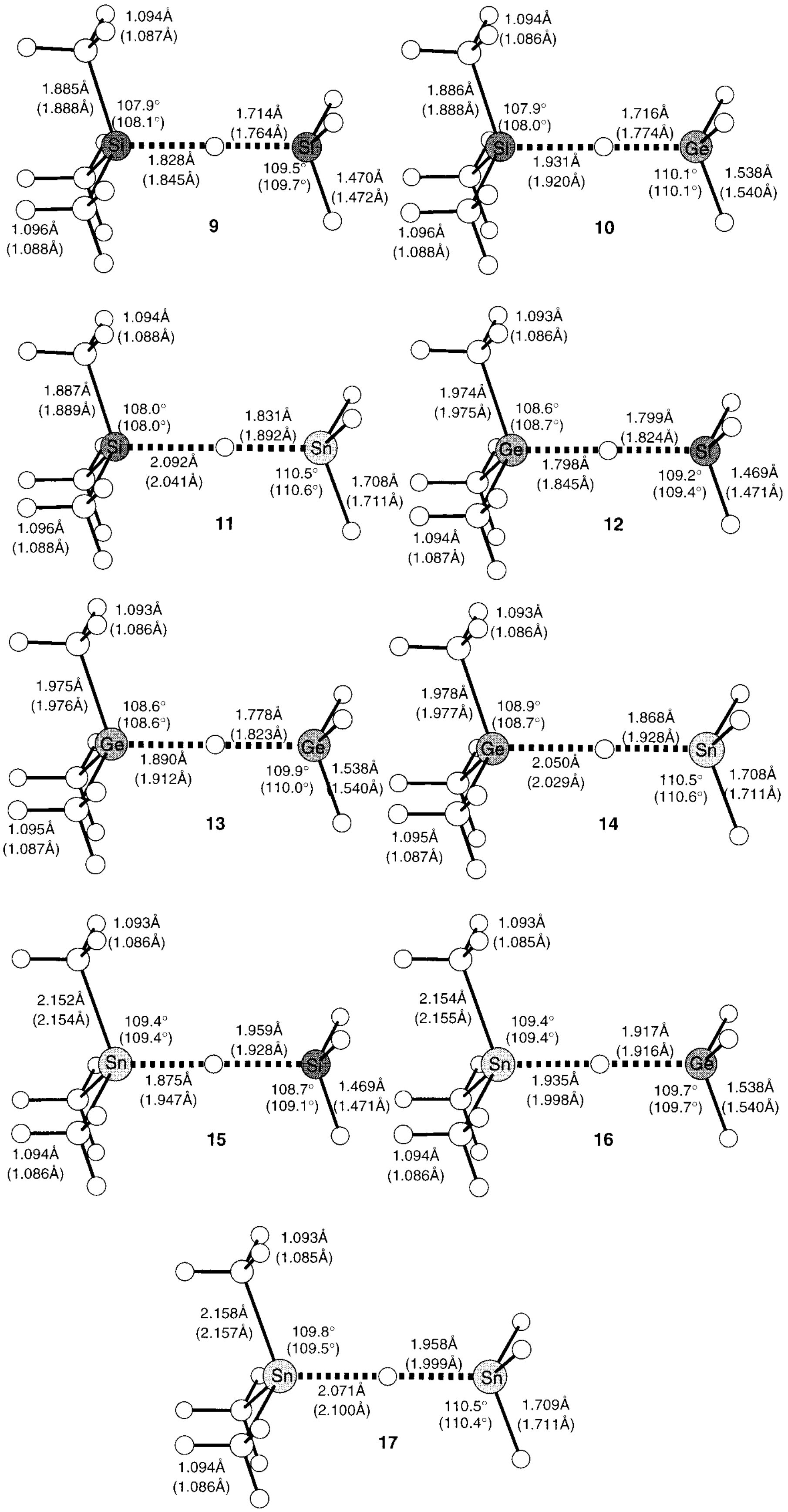
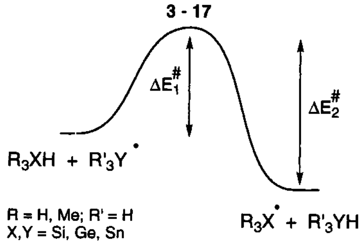


Figure 2.

47.0, and 38.9 kJ·mol^{-1} for the same three reactions, respectively. It is interesting to compare the calculated values of $\Delta E_1^{\#}$ with the limited experimental data available. The correlated values of 53−58 kJ·mol^{-1} for the energy barrier involved in the abstraction of a hydrogen atom from silane by a silyl radical compare

Scheme 2



favorably with the published estimate of more than about 60 kJ·mol^{-1}.[12]

In the asymmetrical exchange reactions involving transition states **6**−**8**, the calculated energy barriers ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$) are consistent with the degree of "lateness" of the reactions in question. For example, transition state **6** is predicted to lie some 38.5 kJ·mol^{-1} above the energy of the silyl radical and germane ($^{\bullet}SiH_3 + GeH_4$) and 65.0 kJ·mol^{-1} above the germyl radical and silane ($^{\bullet}GeH_3 + SiH_4$) at the QCISD/DZP//MP2/DZP (+ ZPVE) level of theory. The lower barrier ($\Delta E_2^{\#}$) associated with the attack of the silyl radical manifests itself in the longer Si−H$_{TS}$ separation in **6** when compared with structure **3**; conversely, the higher $\Delta E_1^{\#}$ is consistent with the shorter Ge−H$_{TS}$ distance. Similar effects are observed in the reactions involving transition states **7** and **8**. As expected, the reaction of the most reactive radical ($^{\bullet}SiH_3$) and the best hydrogen donor (SnH_4)[18,19] is predicted to have the lowest energy barrier of only 23.4 kJ·mol^{-1} (QCISD/DZP//MP2/DZP (+ ZPVE)), with the reverse reaction calculated to require some 86.0 kJ·mol^{-1} at the same level of theory.

The Effect of Alkyl Substitution: Reactions of Silyl, Germyl, and Stannyl Radicals with Trimethylsilane, Trimethylgermane, and Trimethylstannane. To assess the effect of alkyl substitution on hydrogen atom exchange reactions between silicon, germanium, and tin centers, we began to explore the reactions of silyl, germyl, and stannyl radicals with trimethylsilane, trimethylgermane, and trimethylstannane. Due to size restrictions, MP2/DZP frequency and QCISD/DZP single-point calculations were not performed on these systems; previous data (vide supra) indicate close agreement between MP2 and QCISD generated data.

Searching of the $C_3H_{13}XY$ (X, Y = Si, Ge, Sn) potential energy surfaces at SCF/DZP and MP2/DZP levels of theory located structures **9**−**17** as stationary points. Frequency analysis at the lower level confirmed that these structures correspond to the transition states for hydrogen transfer between the heteroatomic centers; optimized transition states are displayed in Figure 2.

Table 2. Calculated Energy Barriers[a] ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$) for the Hydrogen Atom Exchange Reactions between Silyl, Germyl, and Stannyl Radicals and Trimethylsilane, Trimethylgermane, and Trimethylstannane (Scheme 1, R = Me, R′ = H) and the Transition-State (Imaginary) Frequencies (ν)[b] of Structures 9−17

X	Y	TS	method	$\Delta E_1^{\#}$	$\Delta E_1^{\#}$ + ZPVE[c]	$\Delta E_2^{\#}$	$\Delta E_1^{\#}$ + ZPVE[c]	ν
Si	Si	**9**	SCF/DZP	100.6	93.6	90.5	81.9	1769i
			MP2/DZP	67.9	(60.9)	57.8	(49.2)	
Si	Ge	**10**	SCF/DZP	111.3	103.6	70.5	60.7	1622i
			MP2/DZP	81.7	(74.0)	40.0	(30.2)	
Si	Sn	**11**	SCF/DZP	129.3	119.9	53.4	45.6	1361i
			MP2/DZP	107.7	(98.3)	26.5	(18.7)	
Ge	Si	**12**	SCF/DZP	80.0	72.6	100.6	91.0	1705i
			MP2/DZP	47.0	(39.6)	70.4	(60.8)	
Ge	Ge	**13**	SCF/DZP	88.3	80.4	78.3	68.2	1630i
			MP2/DZP	57.4	(49.5)	49.1	(39.0)	
Ge	Sn	**14**	SCF/DZP	103.6	94.2	58.4	50.0	1434i
			MP2/DZP	79.4	(70.0)	31.5	(23.1)	
Sn	Si	**15**	SCF/DZP	60.0	53.5	117.0	105.4	1516i
			MP2/DZP	30.3	(23.8)	94.9	(83.3)	
Sn	Ge	**16**	SCF/DZP	65.2	57.3	91.6	78.7	1530i
			MP2/DZP	35.7	(27.8)	68.6	(55.7)	
Sn	Sn	**17**	SCF/DZP	76.1	68.5	67.4	57.9	1461i
			MP2/DZP	50.4	(42.8)	43.8	(34.3)	

[a] Energies in kJ·mol^{-1}. [b] Frequencies in cm^{-1}. [c] Values in parentheses are estimates based on SCF/DZP ZPVE corrections.

Table 3. SCF, MP2, and QCISD[a] Calculated Energies[b] of the Transition States 3−17 in This Study

structure	SCF/DZP	MP2/DZP	QCISD/DZP
3	−11.524 86	−11.736 32	−11.788 37
4	−11.270 22	−11.475 70	−11.526 71
5	−10.456 63	−10.644 35	−10.694 86
6	−11.397 08	−11.605 35	−11.656 91
7	−10.988 31	−11.186 68	−11.237 99
8	−10.862 60	−11.058 68	−11.109 44
9	−128.689 79	−129.328 57	
10	−128.561 86	−128.197 12	
11	−128.152 65	−128.777 70	
12	−128.553 29	−128.191 39	
13	−128.426 23	−129.061 25	
14	−128.018 09	−128.643 37	
15	−128.141 80	−128.772 49	
16	−128.015 95	−128.644 28	
17	−127.609 42	−128.229 15	

[a] QCISD/DZP//MP2/DZP. [b] Energies in hartrees (1 E_h = 2626 kJ·mol^{-1}).

Inspection of Figure 2 reveals that transition states **9**−**17**, with shorter Me$_3$X−H$_{TS}$ separations than the corresponding structures in Figure 1, are all "later" than the analogous unsubstituted transition states **3**−**8**; this effect is best demonstrated in reactions involving the same heteroatom. The reaction of the silyl radical with trimethylsilane, with Si−H$_{TS}$ distances of 1.714 and 1.828 Å in transition state **9** calculated at the MP2/DZP level, is illustrative of these differences; the Si−H$_{TS}$ distance in **3** is predicted to be 1.757 Å at the same level of theory. Similarly, transition states **13** and **17**, with MP2/DZP generated Ge−H$_{TS}$ and Sn−H$_{TS}$ distances of 1.778 and 1.890 Å (**13**) and 1.958 and 2.071 Å (**17**), display analogous deviations from the unsubstituted transition states; the Ge−H$_{TS}$ distance in **4** is calculated to be 1.820 Å, while the Sn−H$_{TS}$ separation in **5** is 2.002 Å at the same level of theory. The degree of "lateness" exhibited in these reactions manifests itself (as expected) in the energy barriers ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$). At the MP2/DZP (+ ZPVE) level, the forward barriers ($\Delta E_1^{\#}$, Scheme 2) are calculated to be some 8.5−11.7 kJ·mol^{-1} higher in energy than the reverse barriers ($\Delta E_2^{\#}$).

Comparison of the data presented in Tables 1 and 2 reveals that similar trends are predicted for the remaining reactions involving the substitutued silanes, germanes, and stannanes when compared with the unsubstituted systems. These calculations suggest, therefore, that methyl-substituted hydrides are slightly poorer hydrogen donors than their unsubstituted counterparts, in accord with experimental observation.[5,21]

Conclusions

Ab initio calculations predict that the reactions of silyl, germyl, and stannyl radicals with silane, germane, stannane, trimethylsilane, trimethylgermane, and trimethylstannane proceed via transition states of C_{3v} or D_{3d} symmetry in which the attacking and leaving radical centers adopt a collinear arrangement. For reactions involving unsubstituted radical species, energy barriers of between 23.4 ($^\bullet SiH_3 + SnH_4$) and 86.0 ($^\bullet SnH_3 + SiH_4$) $kJ{\cdot}mol^{-1}$ are predicted at the QCISD/DZP//MP2/DZP (+ ZPVE) level of theory.

Inclusion of alkyl substitution on one of the heteroatoms in each reaction serves to alter the position of the hydrogen atom undergoing translocation in the transition state when compared with the unsubstituted series; the reactions of $H_3Y^\bullet$ with Me_3XH become "later" when compared with the analogous parent reaction ($H_3Y^\bullet$ with XH_4). Energy barriers of between 23.8 ($^\bullet SiH_3 + Me_3SnH$) and 98.3 ($^\bullet SnH_3 + Me_3SiH$) $kJ{\cdot}mol^{-1}$ are predicted at the MP2/DZP (+ ZPVE) level of theory.

It is interesting to note that the identity exchange reaction involving silane and the silyl radical is predicted to involve an energy barrier of some 53.6 $kJ{\cdot}mol^{-1}$ at the highest level of theory, in good agreement with the best estimate available (>60 $kJ{\cdot}mol^{-1}$).[12] The similar reaction involving the stannyl radical ($^\bullet SnH_3 + SnH_4$) and the analogous substituted reactions ($^\bullet SnH_3 + Me_3SnH$; $^\bullet SnMe_3 + SnH_4$) are predicted to have associated energy barriers of between 34.3 and 50.4 $kJ{\cdot}mol^{-1}$ at correlated levels of theory, significantly higher than the estimate of about 8 $kJ{\cdot}mol^{-1}$ based on ESR and NMR line-width effects.[11] High barriers are also predicted for the analogous reactions involving germanium (39−50 $kJ{\cdot}mol^{-1}$). Despite the predicted energy barriers being significantly higher than ESR and NMR spectroscopy would suggest, they are consistent with the our silane data and the expectations of Zavitsas and Chatgilialoglu, who state that "the identity reactions $H_3Ge{-}H + {}^\bullet GeH_3$ and $H_3Sn{-}H + {}^\bullet SnH_3$ have not been reported, and we expect that they would have high E_a because of low stretching frequencies of 268 cm^{-1} in Ge−Ge and 192 cm^{-1} in Sn−Sn".[22] We suggest that either solvent plays a dramatic role in these (identity exchange) reactions, a suggestion which is hard to support as the symmetrical transition states **3**−**5** have no dipole, or that rapid hydrogen exchange phenomena are not responsible for the ESR and NMR observations.

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