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Theoretical Study of the Reaction $XY_4 = XY_3+Y$, Where X = C, Si, Ge, Sn, Pb and Y = CH_3, C_2H_5

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A theoretical study of the methyl and ethyl derivatives of C, Si, Ge, Sn, and Pb has been conducted. All-electron basis sets have been used and the relativistic effects taken care with the relativistic elimination of small components (RESC) method, and electron correlation has been taken into account with density functional theory (DFT). A comprehensive set of fully optimized geometries and reaction energies are presented for both methyl and ethyl families. For the methyl derivatives, a more detailed study has been conducted and the following results are juxtaposed: those obtained with two different functionals (BOP and B3LYP) and relativistic vs nonrelativistic. Second, for the methyl derivatives, we also present common thermodynamic quantities as a function of temperature, such as enthalpy, Gibbs' energy, and heat capacity, all of which have been obtained from computing Hessians and using harmonic oscillator and rigid rotor models. Good agreement with experiment is achieved, within a few picometers in optimized geometries and several kcal/mol for reaction energies.

1. Introduction

Recent developments of relativistic methods have facilitated ab initio research of molecules containing heavy elements. With the analytic gradient code available, it is now possible to do a comprehensive study revealing the minimum energy structures and a set of thermodynamic quantities of general interest, such as reaction enthalpies. We chose a recently developed relativistic elimination of small components (RESC)[1,2] method to treat relativistic effects and DFT to handle electron correlation. Second, by using well matched basis sets of uniform quality, we studied relativistic effects, including those for geometry and reaction energy. The reaction we study is a well-known one, with a significant industrial impact: radicalization of tetramethyl and tetraethyl derivatives of elements in group 3-P: C, Si, Ge, Sn, and Pb. Experimental data on the bond dissociation energies for both methyl and ethyl derivatives are available from the review by McMillen and Golden[3]. Almlof and Faegri,[4] in an early study with the Breit-Pauli (BP) Hamiltonian and an all-electron basis set and the first-order perturbation theory to treat relativistic effects, studied the bond energies of the methyl derivatives. A study of the methyl derivatives was also done with effective core potentials by Jonas and Frenking[5] and more recently by Kaupp and Schleyer.[6]

This study provides a comprehensive set of results for both methyl and ethyl derivatives, using all-electron basis sets of uniform quality. The thermodynamical data we provide can be used in simulations of the combustion processes involving tetraethyl lead or other studies.

2. Details of Calculations

There appear to be a few all-electron basis sets available for the whole family of elements C−Pb. We used WTBS basis sets by Klobukowski et al.[7] as a starting point. We then recontracted the primitives with the RESC method by performing atomic restricted ROHF calculations in the uncontracted basis set. Next, we recontracted the lowest (with the largest exponents) 7(C,Si), 6(Ge), 5(Sn), and 4(Pb) *s*-primitives into 1(C,Si) and 2(Ge,Sn,Pb) *s*-functions. To improve the valence and polarization basis we uncontracted the highest 4*s*, 4*p*, 2*d*, and 1*f* functions for each atom. In case *d* or *f* functions had not been present in the original basis for the lighter elements, we optimized the exponents with the configuration interaction with single and double excitations (CISD) method for the lowest atomic term (^2P). These additional exponents were 0.552594 (*d*, C), 0.163904 (*d*, C), 0.787874 (*f*, C); 0.226903 (*d*, Si), 0.057323 (*d*, Si), 0.314081 (*f*, Si); 0.280505 (*f*, Ge); 0.209216 (*f*, Sn). The basis sets thus constructed can be used by others.[8] The basis set used for C and H in CH_3 (Me) and C_2H_5 (Et) fragments was cc-pvdz.[9] Internal uncontraction in the resolutions of the identity, used in RESC, was done only for the central atom X in all compounds XY_n, $n = 3,4$.

For the purpose of emphasing relativistic effects we performed a set of structure optimizations without relativistic corrections to the Hamiltonian. In this case we used original WTBS basis set,[7] which we only partially uncontracted in exactly same fashion as the RESC recontracted basis set described above, so that the two basis sets for each element had exactly same number of basis functions. For the *d* and *f* functions not present in the original WTBS basis set for the lighter elements we used the exponents optimized with RESC. In this way we ensure that the exponent set is the same in both relativistic and nonrelativistic calculations; only the contraction coefficients are different. We consider having two separate basis sets contracted with and without relativity and having the same quality a necessity for fair comparison and deduction of the relativistic effects, provided that contracted basis sets are used. All results presented in this work were obtained with the RESC approach, unless otherwise indicated. No spin−orbit coupling effects were considered. It can be expected that for closed shell tetramethyl and tetraethyl derivatives the effect on geometry and energy is negligibly small, the effect on the radicals can be

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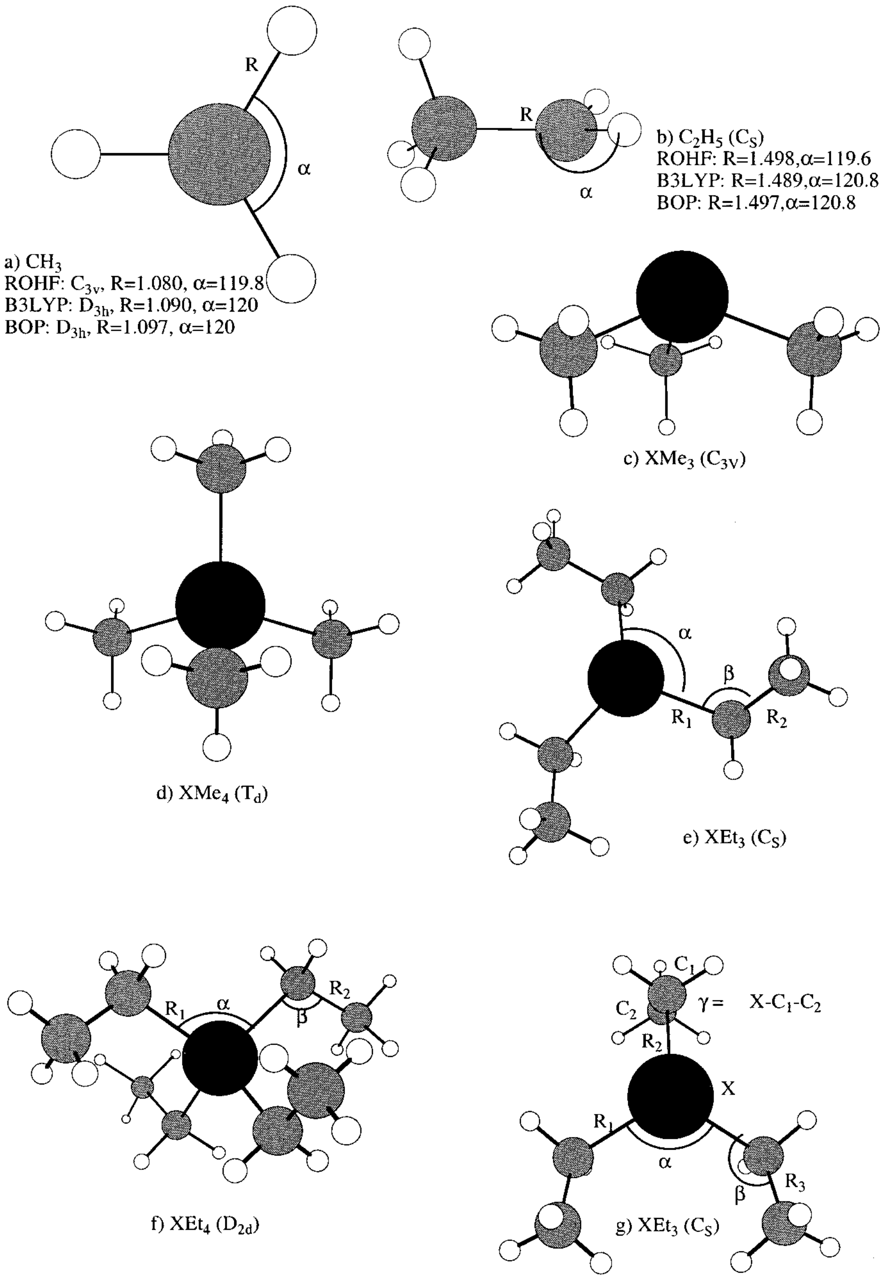

Figure 1. Optimized structures, distances in Å, angles in degrees. Hydrogen atoms are unfilled, carbon atoms are half-filled, and X atoms (X = C, Si, Ge, Sn, Pb) are filled circles. For geometry parameters given symbolically see text.

larger, especially when considering temperature corrections at high temperature.

For all computations we used GAMESS[10] suite of programs. All geometry optimizations were done with a tightened gradient tolerance, set to 10^{-5} and the SCF density convergence was also tightened to 10^{-7}. Two functionals were used in DFT calculations of methyl derivatives: Becke exchange with one-parameter correlation (BOP)[11,12] and B3LYP;[11,13] for ethyl derivatives we only used B3LYP. In all DFT calculations we used a grid $(96(\rho)\times 24(\theta)\times 48(\varphi))$ of higher than the default quality. DFT Hessians were obtained with two-point differencing, and the default step size of 0.01 Å was used, except for the lead derivatives in which case we set it to 0.03 Å to reduce the inaccuracy in the RESC gradients caused by nearly degenerate overlap eigenvalues in the uncontracted basis set.

A geometry optimization search was conducted within several appropriate point groups, and the lowest energy structure was selected. The global minima structures were found to have the following symmetry: T_d for XMe_4, D_{2d} for XEt_4, C_{3v} for Me(ROHF) and XMe_3, D_{3h} for Me(BOP,B3LYP), C_3 for $X'Et_3$ (X' = C(ROHF), Si, Ge, Sn, Pb), and C_s for CEt_3 (BOP, B3LYP) and Et. We note that in case of XEt_3, C_S and C_3 structures for all elements were quite close in energy (different by 0.5−1.5 kcal/mol). In all cases the geometry optimizations were conducted for the ground state, which was the totally symmetric doublet (radicals) or singlet (the rest).

Temperature-dependent properties were computed within the harmonic oscillator, and rigid rotor approximations by using the usual statistical thermodynamics method of partial sums. In the partial sums no contribution from excited electronic states was added. All properties are computed for the gas phase at 1 atm, even at low temperature.

3. Results and Discussion

A. Discussion of Individual Systems. *Electron Correlation Effects.* Schematic structures of all molecules are given in Figure

TABLE 1: Optimized Geometry of XMe_4: R(X−C), Å

X	HF/RESC[a]	BOP/RESC[a]	B3LYP/RESC[a]	HF/BP[4]	HF/ECP[5]	exp
C	1.535	1.553	1.537	1.540	1.535	1.539[16], 1.537[17]
Si	1.901	1.914	1.896	1.902	1.879	1.888[18], 1.875[19]
Ge	1.963	1.993	1.969	1.970	1.972	1.98[20], 1.945[21]
Sn	2.163	2.200	2.172	2.150	2.150	2.182[20], 2.144[22]
Pb	2.232	2.296	2.256	2.247	2.198	2.29[20], 2.203[23], 2.238[24]

[a] This work.

TABLE 2: Optimized Geometry of XMe_3

	HF		BOP		B3LYP	
X	R(X−C), Å	∠C−X−C, °	R(X−C), Å	∠C−X−C, °	R(X−C), Å	∠C−X−C, °
C	1.503	117.3	1.504	117.3	1.494	117.3
Si	1.900	110.4	1.920	110.4	1.901	110.4
Ge	1.972	109.8	2.010	109.5	1.983	109.7
Sn	2.172	108.8	2.227	108.8	2.192	108.8
Pb	2.250	108.4	2.342	106.1	2.293	106.1

TABLE 3: B3LYP Optimized Geometry of XEt_4[a]

X	R(X−C), R_1	R(C−C), R_2	∠C−X−C, α	∠X−C−C, β
C	1.553 (1.551)	1.533 (1.530)	106.3 (106.1)	117.4 (117.6)
Si	1.910 (1.910)	1.538 (1.534)	107.4 (107.0)	116.9 (116.4)
Ge	1.984 (1.975)	1.535 (1.533)	108.2 (107.4)	110.1 (115.6)
Sn	2.191 (2.177)	1.535 (1.533)	109.2 (108.3)	114.3 (115.3)
Pb	2.281 (2.248)	1.531 (1.530)	110.1 (108.9)	113.8 (114.6)

[a] RHF optimized geometry is shown in parentheses. Distances are given in Å, and angles are in degrees. See Figure 1 for the symbols used (R_1, R_2, α, β).

TABLE 4: B3LYP Optimized Geometry of XEt_3 in C_s Symmetry[a]

X	R(X−C): R_1, R_2	R(C−C), R_3	∠C−X−C, α	∠X−C−C: β, γ
C	1.500,1.500	1.546	121.4	114.4, 113.1
Si	1.917, 1.915	1.543	113.0	115.0,116.9
Ge	2.001, 1.998	1.537	111.5	115.7,113.8
Sn	2.216, 2.213	1.533	109.2	115.8, 113.3
Pb	2.321,2.321	1.528	107.11	115.2,112.9

[a] Distances are given in Å and angles are in degrees. See Figure 1 for the symbols used (R_1, R_2, R_3, α, β, γ).

TABLE 5: B3LYP Optimized Geometry of XEt_3 in C_3 Symmetry[a]

X	R(X−C), R_1	R(C−C), R_2	∠C−X−C, α	∠X−C−C, β
C	1.505	1.535	118.1	116.56
Si	1.915	1.536	110.2	115.73
Ge	1.998	1.532	109.4	114.76
Sn	2.187	1.536	110.2	115.76
Pb	2.320	1.526	106.4	114.61

[a] Distances are given in Å and angles are in degrees. See Figure 1 for the symbols used (R_1, R_2, α, β).

TABLE 6: Enthalpies of the Reaction $XY_4 = XY_3 + Y$, kcal/mol

	CH_3		C_2H_5	
X/Y	calc (B3LYP), 298.15 K	exp[3], 298.15 K	calc (B3LYP), 0 K	exp[3], 298.15 K
C	80.0	84 ± 1	77.0	79 ± 1
Si	85.4	89 ± 3	81.3	
Ge	74.0	83 ± 4	72.0	
Sn	65.4	71 ± 4	60.7	63 ± 4
Pb	52.6	57 ± 4	48.7	55 ± 4

TABLE 7: B3LYP Dipole Moments at the Center of Mass, in Debye[a]

X	XMe_3, C_{3V}; μ_Z	XEt_3, C_3; μ_Z	XEt_3, C_S; μ_X, μ_Y
C	0.264	0.262	0.003, 0.040
Si	0.727	0.783	0.510, 0.631
Ge	0.612	0.703	0.459, 0.572
Sn	0.291	0.466	0.332, 0.376
Pb	0.035	0.270	0.216, 0.239

[a] C_{3v} and C_3 molecules are along the *z*-axis and C_s molecules are in the *xy*-plane.

1. Bond distances for the tetramethyl derivatives are summarized in Table 1 and compared to the available experimental and other theoretical data. We note fairly close agreement to the work done by others; given the ambiguity of the experimental data, it is somewhat difficult to judge whose calculation are closer. We observe that B3LYP results show the closest agreement to the experimental geometry. While BOP overestimates the bond length, B3LYP and RHF give both over- and underestimates. In all cases the bond length becomes longer as one goes down the periodic table. This is a general trend and it will be covered at greater length below.

Geometry for trimethyl derivatives is summarized in Table 2. As in the case of tetramethyl compounds, the B3LYP method gives bond distances shorter than BOP by several picometers, while the angle is almost the same. Geometry for tetraethyl derivatives is given in Table 3. We observe that B3LYP gives longer bond distance than RHF. This can be explained by electron correlation that tends to destabilize the bonding relative to RHF. In Tables 4 and 5 we give geometry for triethyl derivatives, for the structures in C_3 and C_s symmetry, respectively. We notice that only CEt_3 has the minimum of C_s symmetry, and other triethyl derivatives have a lower energy minimum in C_3, although in all cases the energy difference is small. CEt_3 having different minima can be due to the smaller size of the carbon atom and a stronger bonding to the ethyl fragments. As can be seen from Tables 4 and 5, the X−C bond distance and the C−X−C angle change considerably from C to Pb. Calculated (B3LYP) and experimental reaction energies are given in Table 6. Quite close correspondence between theoretical and experimental data is seen with all trends correctly reproduced; methyl compounds have stronger X−C bond due to smaller substituent repulsion. Nonzero dipole moments are summarized in Table 7. The general trend is decreasing of the dipole moment from C to Pb. This is due to reduced electron density of the unpaired electron on the central atom X, due to increased metal character; second, the total dipole moment is measured relative to the center of mass so that with heavier nuclei the point of reference is shifted closer to the nuclei, and the nuclear contribution decreases.

B. Discussion of the Radicalization Energies and Other Properties. Demethylation enthalpies are given in Figure 2,

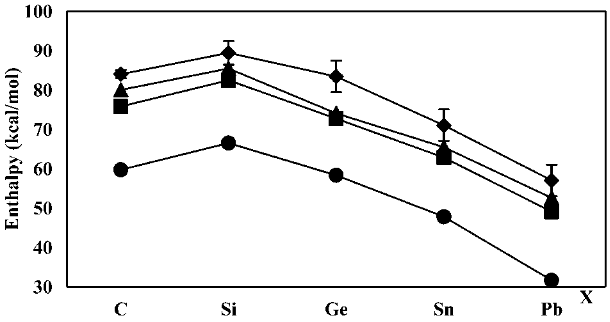

Figure 2. Enthalpies of the reaction $XMe_4 = XMe_3 + Me$ at $T = 298.15$ K: HF (circles), BOP (squares), B3LYP (triangles), and experiment (diamonds). Experimental uncertainty is shown with brackets.

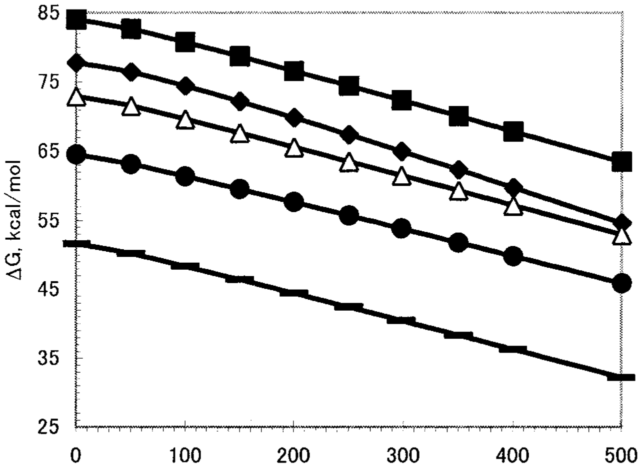

Figure 3. B3LYP Gibbs' energies for the reaction $XMe_4 = XMe_3 + Me$: C (filled diamonds), Si (filled squares), Ge (open triangles), Sn (filled circles), Pb (filled dashes).

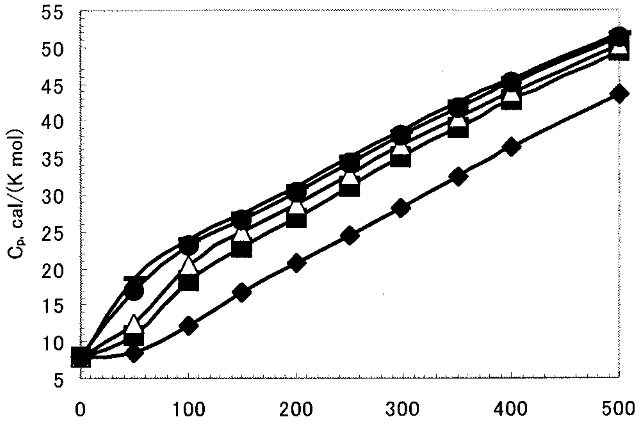

Figure 4. B3LYP values of C_P for XMe_4: X = C (filled diamonds), Si (filled squares), Ge (open triangles), Sn (filled circles), Pb (filled dashes).

Gibbs' energies in Figure 3, and heat capacities for the tetramethyl compounds in Figure 4. Temperature correction was obtained with partial sums based on numeric Hessians, and zero point energy (ZPE) is included in the vibrational partial sum. Ethyl radicalization energies are given in Figure 5. No Hessians were computed and thus the energies are given at 0 K without ZPE and temperature correction.

We observe good agreement of reaction enthalpies with experiment in both cases of methyl and ethyl derivatives. The closest agreement is obtained with B3LYP, and HF significantly underestimates the reaction enthalpies by about 20−25 kcal/mol. In case of the methyl radicalization, B3LYP underestimates the experimental value at room temperature by about 5 kcal/mol and the disagreement is slightly larger for germanium. For methyl compounds the temperature correction decreases the reaction enthalpy by about 4−6 kcal/mol. It can be expected that for ethyl derivatives such correction will be similar but slightly smaller (1 kcal/mol or less) due to smaller difference in ZPE, which occurs because of smaller difference in vibrational energies of the ethyl tetra- and tri- derivatives as compared to those for the methyl derivatives. Thus we can expect the reaction enthalpy for ethyl derivatives to be several kcal/mol smaller at room temperature, and with this assumption we see that the agreement between B3LYP and experimental data is quite good and the difference is again about 5−7 kcal/mol, except for lead where it is a several kcal/mol larger.

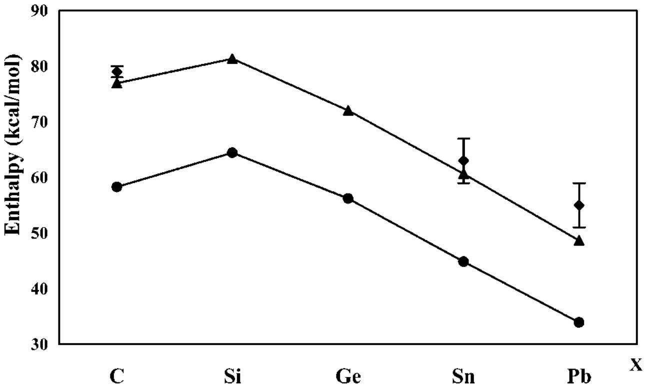

Figure 5. Enthalpies of the reaction $XEt_4 = XEt_3 + Et$: HF (circles), B3LYP (triangles), and experiment (diamonds). Experimental results at T = 298.15 K and theoretical results (without ZPE) at 0 K. Experimental uncertainty is shown with brackets.

TABLE 8: Calculated Nonrelativistic (NR) and Relativistic (RESC) Optimized X−C Bond Distances in XMe_4, Reaction Energies of $XMe_4 = XMe_3 + Me$ at 0 K (no ZPE correction is included)

	R(X−C), Å			dissociation energy, kcal/mol		
X (method)	NR	RESC	Δ[a]	NR	RESC	Δ[a]
C (HF)	1.535	1.535	0.000	66.10	66.06	−0.04
C (B3LYP)	1.538	1.537	−0.001	86.06	86.04	−0.02
C (BOP)	1.553	1.553	0.000	81.77	81.76	−0.01
Si (HF)	1.898	1.901	0.003	70.62	70.46	−0.16
Si (B3LYP)	1.897	1.896	−0.001	89.30	89.12	−0.18
Si (BOP)	1.914	1.914	0.000	86.37	86.19	−0.14
Ge (HF)	1.968	1.963	−0.005	62.99	62.20	−0.79
Ge (B3LYP)	1.973	1.969	−0.004	80.73	77.78	−2.95
Ge (BOP)	1.995	1.993	−0.002	77.67	76.55	−0.12
Sn (HF)	2.177	2.163	−0.014	53.22	51.30	−1.92
Sn (B3LYP)	2.182	2.172	−0.010	71.41	68.84	−2.57
Sn (BOP)	2.207	2.200	−0.007	68.91	66.15	−2.76
Pb (HF)	2.280	2.232	−0.048	46.09	39.87	−7.22
Pb (B3LYP)	2.285	2.256	−0.029	64.57	56.32	−8.25
Pb (BOP)	2.313	2.296	−0.017	62.28	53.49	−8.79

[a] The difference between RESC and NR values.

C. Discussion of Relativistic Effects. We provide detailed summary of relativistic effects in Table 8. Only methyl derivatives were included in these calculations, and no temperature correction is included. The X−C bond distance is shortened by relativity, up to about 0.05 Å or 5% in Pb, whereas the dissociation energy is decreased, up to about 10 kcal/mol or 7% in Pb. This is consistent with the review by Pyykkö.[14] Relativistic contraction of s and p orbitals appears to shorten the bond length and destabilize bonding due to increased repulsion. In almost all cases we observe that relativistic effects on the dissociation energy for the single reference wave function (HF) are smaller than those for the DFT calculations. This suggests that electron correlation is significantly affected by adding relativistic effects, and this results in the further bond shortening and bond energy decrease. For C to Sn compounds, the electron correlation and the relativistic effects to the bond length are comparable in magnitude and have opposite sign. Thus the nonrelativistic HF bond length is close to the RESC−B3LYP bond length. For Pb, however, the relativistic effects become larger than the correlation effects and the X−C bond length is significantly decreased by the relativity. Bond dissociation energies are increased due to the electron correlation effects for all central atoms X. In most cases with the exception of Ge there is little difference between relativistic effects for BOP and B3LYP.

D. Discussion of Periodic Trends. Comparing the results for all atoms X (X = C, Si, Ge, Sn, Pb), several trends are observed. The bond distance becomes longer by about 0.76 Å, and the bond dissociation energy decreases by about 35 kcal/mol. This is consistent with the increased metallic character of the heavier elements that takes its roots in stronger shielding of the valence by the core electrons. As clearly seen in Figures 2 and 5, a very often observed “cusp” at the second row is seen. It can be explained by noting that the shielding for the first row has a different character compared to other atoms, namely, it involves only spherically symmetric s electrons. From the second row (e.g., Si, in this case) down, the shielding of the valence p electrons is exerted by the p-like electrons in the core. Another source of the cusp is the presence of the virtual d electrons that become quite important for electron correlation in derivatives of Si and other heavier atoms. It can be noticed that the cusp is observed at the HF level as well, thus this additional factor of the influence of d electrons seems to be less relevant; these observations are in agreement with Kutzelnigg.[15] The same trend of the first row having different properties from the rest is observed in transition metals.

It is interesting to note that the heat capacities plotted in Figure 4 are not as different as other properties, such as reaction enthalpies for all five elements. This may be due to the somewhat similar vibrational energy of all tetramethyl derivatives that contributes most to the heat capacities (except at very low temperature, where translational and rotational energies prevail, also similar for all tetramethyl derivatives). More difference is observed in the intermediate range of temperature, where the relative difference is large.

4. Conclusions

We presented a comprehensive set of results for methyl and ethyl derivatives of elements C−Pb, including fully optimized structures, radicalization enthalpies, dipole moments, and important thermodynamic quantities as a function of temperature. Consistent with available experimental results, tetraethyl lead is found to have the smallest reaction enthalpy and thus to be the most efficient fuel additive; tetraethyl tin is found to be the next candidate, however, its significantly higher value makes its much less efficient. Good agreement is achieved when compared to the experiment, and the best results are obtained with the B3LYP functional. Relativistic corrections incorporated with RESC proved to work reasonably well. Further improvements can be achieved through a higher level of electron correlation or a better functional. Temperature effects can be better incorporated with the inclusion of anharmonicity. Spin−orbit coupling effects on the radical structure and energy can improve the results, especially at higher temperature. Given the experimental uncertainty and contradicting data, we assume the results presented here are of good quality and can be used for some further modeling of the radicalization reaction studied.

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References and Notes

(1) (a) Nakajima, T.; Hirao, K. *Chem. Phys. Lett*. **1999**, *302*, 383. (b) Fedorov, D. G.; Nakajima, T.; Hirao, K. *Chem. Phys. Lett*. **2001**, *35*, 183.

(2) The RESC Hamiltonian was found to be variationally unstable (Barysz, M. *J. Chem. Phys*. **2000**, *113*, 4003) if very large exponents are used for heavy elements; however, as the above reference also notes, in general, the RESC approach is suitable for calculations of chemically important relative energies. No evidence of variational collapse was found in this work.

(3) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem*. **1982**, *33*, 493.

(4) Almlof, J., Faegri, K., Jr. *Theor. Chim. Acta* **1986**, *69*, 437.

(5) Jonas, V.; Frenking, G. J. *Comput. Chem*. **1992**, *13*, 935.

(6) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc*. **1993**, *115*, 1061.

(7) Huzinaga, S.; Klobukowski, M. *Chem. Phys. Lett*. **1993**, *212*, 260.

(8) http://www.appchem.t.u-tokyo.ac.jp/appchem/labs/hirao/publications/basisset/mwtbs-14.html.

(9) Dunning, T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007.

(10) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem*. **1993**, *14*, 1347.

(11) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(12) Tsuneda, T.; Suzumura, T.; Hirao, K. *J. Chem. Phys*. **1999**, *110*, 10664.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Stevens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(14) Pyykkö, P. *Chem. Rev*. **1988**, *88*, 563.

(15) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl*. **1984**, *23*, 272.

(16) Beagley, B.; Brown, D. P.; Monhagen, J. J. *J. Mol. Struct*. **1969**, *4*, 233.

(17) Bartel, L. S.; Bradford, W. F. *J. Mol. Struct*. **1977**, *37*, 113.

(18) Wells, A. F. *Structural Inorganic Chemistry*, Oxford University Press: Oxford, 1962.

(19) Beagley, B.; Monhagen, J. J.; Hewitt, T. G. *J. Mol. Struct*. **1971**, *8*, 401.

(20) Brockway, L. O.; Jenkins, H. O. *J. Am. Chem. Soc.* **1936**, *58*, 2036.

(21) Hencher, J. L.; Mustol, F. J. *Can. J. Chem*. **1975**, *53*, 3542.

(22) Nagashima, M.; Fujii, H.; Kimura, M. *Bull Chem. Soc. Jpn*. **1973**, *46*, 3708.

(23) Wong, C. H.; Schomaker, V. *J. Chem. Phys*. **1958**, *28*, 1007.

(24) Oyamada, T.; Lijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn*. **1971**, *44*, 2638.