

Examining Trends in the Tetravalent Character of Group 14 Elements (C, Si, Ge, Sn, Pb) with Acids and Hydroperoxides

Nancy A. Richardson,[†] Jonathan C. Rienstra-Kiracofe,[‡] and Henry F. Schaefer, III*

Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602-2525

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Abstract: The shift from tetravalency to divalency in going from carbon to lead chemistry is thought to be one of the most striking periodic properties. Although several molecules in the series $R-(X=O)-OH$ and $R-\ddot{X}-O-OH$ ($R = H, CH_3$; $X = C, Si, Ge, Sn, Pb$) have been synthesized, most are unknown to date. Using density functional theory and hybrid Hartree-Fock/density functional theory with the BLYP and B3LYP functionals, the relative stability of hydroperoxycarbene, ($H-\ddot{C}-O-O-H$) to its acid isomer, formic acid, is predicted to be +96.4 kcal/mol with BLYP and a triple- ζ plus double polarization (TZ2P) basis set. As other group 14 atoms replace the carbon atom, this energy difference lessens considerably: Si, 101.0 (TZ2P) and 92.1 (TZ2P-ECP); Ge, 57.0 (TZ2P), and 65.5 (TZ2P-ECP); Sn, 48.4 (TZ2P-ECP); Pb, 22.1 (TZ2P-ECP), where TZ2P-ECP indicates that effective core potentials (ECP) were used for the group 14 atom only. As one descends group 14, the acid form remains lower in energy than the peroxide form, indicating that even for lead tetravalency is preferred. A similar trend occurs for the relative energies between the group 14 congeners of hydroperoxymethylcarbene ($CH_3-\ddot{C}-O-O-H$) and its acid isomer, acetic acid: C, 88.1 (TZ2P); Si, 101.9 (TZ2P) and 93.1 (TZ2P-ECP); Ge, 58.7 (TZ2P) and 67.2 (TZ2P-ECP); Sn, 50.4 (TZ2P-ECP); Pb, 25.1 (TZ2P-ECP). Results with B3LYP were similar to those of BLYP though the former are somewhat more dubious due to spin contamination in the carbon congeners. Coupled cluster singles and doubles (CCSD) and CCSD with triple excitations perturbatively added (CCSD(T)) single-point energies also show similar results and favor the tetravalent acid congeners by 4–13 kcal/mol more than density functional theory.

Introduction

The atmospheric pollutant gases methyl hydroperoxide (CH_3OOH) and ethyl hydroperoxide (CH_3CH_2OOH) play an important role in atmospheric and combustion chemistry.¹ The hydroperoxyalkyl radicals ($\cdot C_nH_{2n}OOH$) have been proposed as intermediates in the combustion of alkanes.² However, the corresponding carbene hydroperoxides, hydroperoxycarbene ($H\ddot{C}OOH$) and hydroperoxymethylcarbene ($CH_3\ddot{C}OOH$), which are isomeric to formic acid and acetic acid, have not been observed. Carbon's preference for tetravalency over divalency strongly suggests that the acids are inherently more stable. However, the group 14 elements in later periods often tend toward divalency.^{3,4} In the isovalent group 14 formaldehyde series (molecules of the form H_2XO), Kapp, Remko, and Schleyer found that all of the species except $X = C$ exhibited a global minimum with the divalent $H-\ddot{X}-O-H$ carbene-like species,^{5,6} though tetravalent $H_2Si=O$ may actually be slightly more stable than its divalent isomer.⁷ Other similar germanium

species (H_2GeX , $X = S, Se$) all favor divalency.⁸ Interestingly, Kapp et al. indicated that the presence of methyl groups stabilizes metal $X=O$ double bonds. Furthermore, in an earlier study, Kaupp and Schleyer noted that electronegative substituents (specifically, F and Cl) significantly destabilize tetravalent lead compounds.^{9,10} Thus one might expect the divalent hydroperoxides ($H\ddot{X}OOH$, $CH_3\ddot{X}OOH$) of silicon, germanium, tin, and lead to be more stable than the tetravalent acids, which have electronegative O and OH functional groups.¹¹ In addition, one might expect the acetic acid congeners to be relatively more stable than the formic acid congeners when compared to their divalent carbene-like isomers, due to the presence of a methyl substituent.

The preference for tetravalency or divalency in group 14 atoms is likely very dependent upon the nature of the substituents. To examine the preference of group 14 atoms for tetravalency or divalency when the one of the substituents is a hydroperoxy group, this paper studies the relative stability of

[†] Current address: Pensacola Christian College, Box 18000, Pensacola, FL 32503.

[‡] E-mail: rienstra@ccqc.uga.edu.

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the group 14 acids analogous to formic and acetic acid and their corresponding hydroperoxide carbene-like isomers.

Many of the molecules in this series are not known experimentally and have not been studied theoretically. However, they are closely related to molecules that have been observed experimentally, and comparison between the congeners studied here may provide a better understanding of more commonly known and studied species. Silanoic acid has been observed experimentally and is well characterized, as are related molecules such as silanol, silanone, and silicic acid.^{12,13} The hydroperoxy isomer of silanoic acid, H–Si–O–O–H has been studied as a possible intermediate in silane combustion^{14–16} and was predicted by Darling and Schlegel to be less stable than silanoic acid by more than 100 kcal/mol using G2 theory.¹⁴ The methyl-substituted silanoic acid anion, CH₃SiO₂[−], has also been observed.^{17,18} To the best of our knowledge, the next congener in the series, germanonic acid, is unknown, and the hydroperoxy isomer of germanonic acid, H–Ge–O–O–H, is also uninvestigated. The related tetravalent molecule, trimethylgermyl hydroperoxide (Me₃GeOOH), was proposed in 1994 by Harrison and Poesta to be an intermediate in the autoxidation of trimethylgermane¹⁹ and other hydroperoxy–germanium species are known.²⁰ For the tin and lead congeners, we find no experimental or theoretical work on either the acid or the hydroperoxide. However, many divalent and tetravalent compounds are known and characterized for both lead and tin.^{3,4,21}

Theoretical Methods

Absolute energies, optimized geometries, and harmonic vibrational frequencies were determined using density functional theory (DFT) for each molecule studied. Two exchange-correlation density functionals were used and are denoted by B3LYP and BLYP. These are generalized gradient approximations and employ the dynamical correlation functional of Lee, Yang, and Parr (LYP)²² in conjunction with one of Becke's exchange functionals: the three-parameter HF/DFT hybrid exchange functional (B3)²³ for B3LYP or the pure DFT exchange functional (B)²⁴ for BLYP. The Gaussian94 system of DFT programs²⁵ was used for all results. The OPT=TIGHT parameter was used in geometry optimizations. The coupled cluster with single- and double-excitations (CCSD) method^{26–28} and the CCSD with perturbative triple-

excitations CCSD(T) method^{29,30} were used to generate single-point energies at the BLYP/TZ2P and BLYP/TZ2P-ECP optimized geometries. The ACES II program³¹ was employed for the coupled cluster results.

A restricted reference was used in all cases, except where indicated. Harmonic vibrational frequencies were determined at the DZP and/or DZP-ECP level of theory for both B3LYP and BLYP. Frequencies were computed analytically for the all-electron basis set (DZP) and via finite differences of analytic first derivatives for effective core potential (ECP) basis sets (DZP-ECP).

Specifically, three basis sets were used. For all of the atoms in the C and Si congeners as well as all H, C, and O atoms in the other congeners, we employed a double- ζ basis set with single polarization functions (DZP) which was originally constructed from the Huzinaga–Dunning^{32,33} set of contracted double- ζ Gaussian functions and augmented with one set of p polarization functions for each H atom and one set of five d polarization functions for each C, O, and Si atom [α_p (H) = 0.75, α_d (C) = 0.75, α_d (O) = 0.85, and α_d (Si) = 0.50]. We also employed the triple- ζ Gaussian functions of Dunning^{34,35} augmented with two sets of p polarization functions for each H atom and two sets of five d polarization functions for each C, O, and Si atom [α_p (H) = 1.50 and 0.375, α_d (C) = 1.50 and 0.375, α_d (O) = 1.70 and 0.425, and α_d (Si) = 1.00 and 0.25]. For Ge, the triple- ζ basis set of Dunning³⁶ augmented with one set of five d polarization functions where α_d (Ge) = 0.25 was used. This basis set for Ge, which can be denoted as Ge(14s11p6d/10s8p3d), was used whether the remaining atoms employed a DZP or TZ2P basis set. Additionally a third basis set for the congeners of Si, Ge, Sn, and Pb was employed. In this instance, the central group 14 atom used a valence double- ζ basis and with an ECP as given by the LANL2DZ basis set.^{37–39} These ECPs incorporate Darwin and mass–velocity relativistic effects. When the ECP was used for the central atom, the remaining atoms employed the all-electron DZP or TZ2P basis sets. These hybrid basis sets are denoted DZP-ECP and TZ2P-ECP, respectively. No d functions were added to the ECP basis sets, however, d valence participation is expected to be small in these molecules.⁵ Molecular spin–orbit effects were not considered (except where noted) and are expected to be small for closed-shell species.^{40–43}

Finally, it should be noted that the B3 exchange functional is a parametrized functional and has been fit only to first- and second-row compounds.²³ Thus we might expect the B3LYP results to be less accurate for investigations of Ge-, Sn-, and Pb-containing species.

Atomic charges and bond orders were determined using the natural bond order (NBO) analysis of Reed and Weinhold.^{44–47} Analysis was done at the B3LYP/DZP and B3LYP/DZP-ECP levels.

Results and Discussion

Full geometry optimizations of various conformations of formic acid, hydroperoxycarbene, acetic acid, and hydroper-

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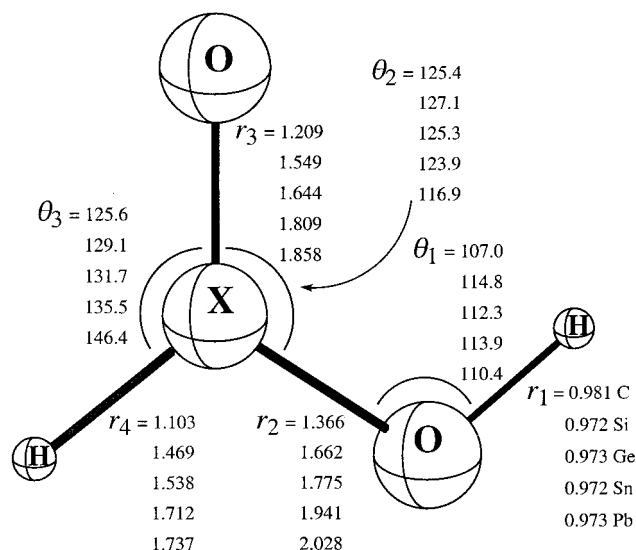


Figure 1. Lowest energy conformation for the group 14 congeners of formic acid, where X = C, Si, Ge, Sn, Pb. BLYP/TZ2P optimized geometries are shown for X = C and BLYP/TZ2P-ECP geometries for X = Si–Pb. All congeners have C_s symmetry and a $^1A'$ electronic ground state.

oxymethylcarbene resulted in several minimums for each species at the DZP level with both B3LYP and BLYP. All minimums found for formic acid, acetic acid, hydroperoxycarbene, and hydroperoxymethylcarbene have C_s symmetry except the lowest energy minimum of hydroperoxymethylcarbene, which has C_1 symmetry.

The lowest energy cis conformation of formic acid is shown in Figure 1. A second trans conformer of formic acid lies 5.1 and 4.9 kcal/mol higher with B3LYP and BLYP, respectively, and has the O–H bond rotated by 180° with respect to the structure shown in Figure 1. This energy increase is expected since the interaction of the hydrogen atom with the carbonyl oxygen provides stabilization for the cis conformer. This stabilization is in agreement with other experimental and theoretical results.^{48–50} It should also be noted that previous theoretical work on silanoic acid shows it also has a global cis conformation.^{14,51,52}

The hydroperoxycarbene species has three minimums, the lowest of which is shown in Figure 2. Two others lie 10.3 and 11.5 kcal/mol higher in energy with B3LYP and 13.9 and 12.2 kcal/mol higher in energy for BLYP. In the second minimum of hydroperoxycarbene, both the C–H bond and the O–H bond are rotated 180° , while in the third minimum, just the O–O bond is rotated 180° with respect to Figure 2.

Acetic acid exhibited two minimums as well as one transition state. The structure of the lowest cis minimum is shown in Figure 3. Like formic acid, the second trans conformer of acetic acid has the hydroxy O–H bond rotated 180° from that shown

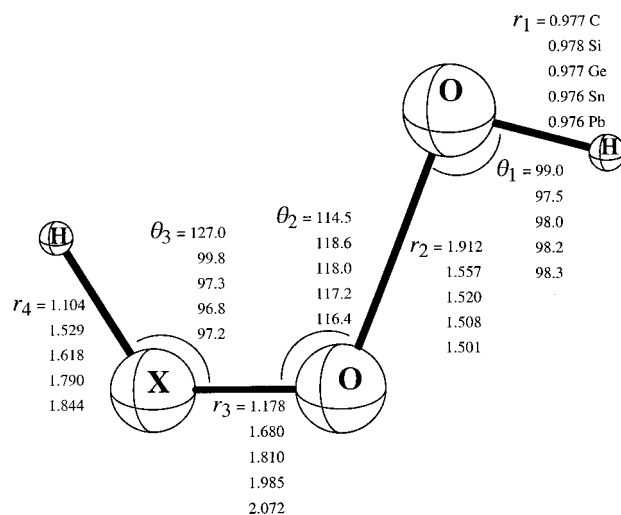


Figure 2. Lowest energy conformation for the group 14 congeners of hydroperoxycarbene, where X = C, Si, Ge, Sn, Pb. BLYP/TZ2P optimized geometries are shown for X = C and BLYP/TZ2P-ECP geometries for X = Si–Pb. All congeners have C_s symmetry and a $^1A'$ electronic ground state.

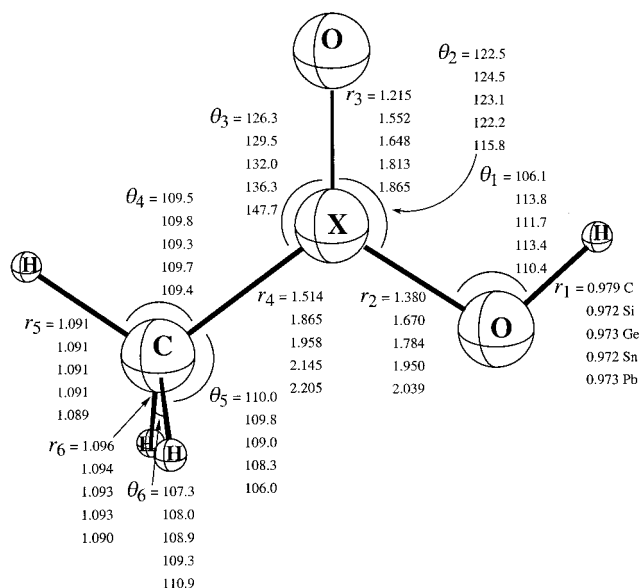


Figure 3. Lowest energy conformation for the group 14 congeners of acetic acid, where X = C, Si, Ge, Sn, Pb. BLYP/TZ2P optimized geometries are shown for X = C and BLYP/TZ2P-ECP geometries for X = Si–Pb. All congeners have C_s symmetry and a $^1A'$ electronic ground state.

in Figure 3. This minimum lies 5.9 and 5.5 kcal/mol higher in energy with B3LYP and BLYP, respectively. Compared to the lowest energy acetic acid structure, a transition state was found that lies 0.26 and 0.17 kcal/mol higher with B3LYP and BLYP, respectively. In this structure, the methyl group is rotated 180 degrees and the imaginary normal mode corresponds to rotation of the methyl group, indicating that the methyl group is essentially a free rotor.

In hydroperoxymethylcarbene, the lowest minimum is predicted to be of C_1 symmetry with a C–O–O–H torsion angle of ~ -12 degrees; this species is shown in Figure 4. Two other minimums, **A** and **B**, both of C_s symmetry, were found and are shown in Figure 5. **A** lies 17.4 and 16.8 kcal/mol above hydroperoxymethylcarbene with B3LYP and BLYP, respectively, and **B** lies 16.1 and 18.7 kcal/mol higher with B3LYP and BLYP, respectively.

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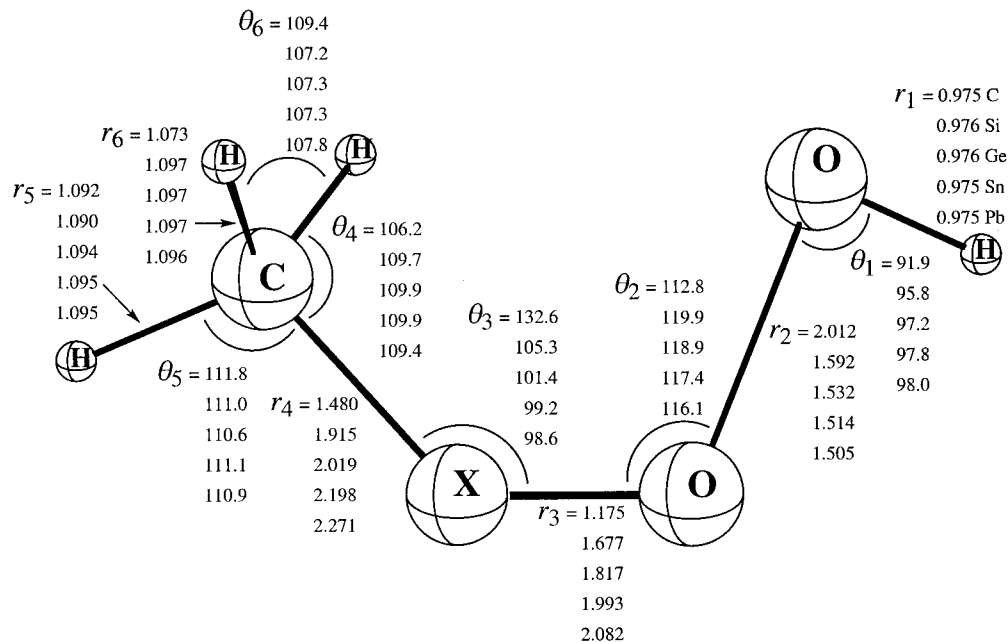


Figure 4. Lowest energy conformation for the group 14 congeners of hydroperoxymethylcarbene, where X = C, Si, Ge, Sn, Pb. BLYP/TZ2P optimized geometries are shown for X = C and BLYP/TZ2P-ECP geometries for X = Si–Pb. Hydroperoxymethylcarbene (X = C) has C_1 symmetry and a 1A electronic ground state. The other congeners have C_s symmetry and $^1A'$ electronic ground states.

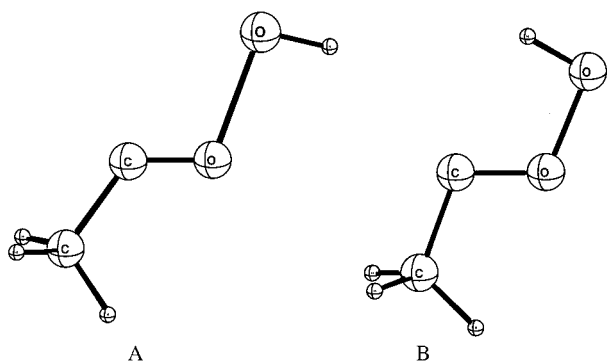


Figure 5. Two higher energy minima of hydroperoxymethylcarbene. Both conformations have C_s symmetry and $^1A'$ electronic ground states.

The lowest energy minima of formic acid, acetic acid, and hydroperoxycarbene all have $^1A'$ electronic ground states while hydroperoxymethylcarbene has a 1A electronic ground state.

Electronic Structure Considerations. Density functional theory has been shown to provide reasonable results for many ground-state singlet carbenes.^{53,54} However, since many carbenes may have other important low-lying electronic states, the accuracy of a restricted single determinant in describing the hydroperoxides in this study was important to investigate. The lowest energy hydroperoxy and hydroperoxymethyl carbenes geometries, shown in Figures 2 and 4, were optimized in an unrestricted formalism. In each case, the converged solution resulted in the singlet state. However, for these singlet carbene molecules, the B3LYP results have significant spin contamination with the expectation value of S^2 being 0.78 for hydroperoxycarbene and 0.69 for hydroperoxymethylcarbene. For BLYP, no unrestricted solution was found in either carbene.

It is interesting to compare the energies and geometries of the unrestricted B3LYP solution to those of the restricted B3LYP solution for hydroperoxycarbene. The O–O bond length

with RB3LYP, $r(\text{O}–\text{O}) = 1.78 \text{ \AA}$, is significantly shorter than the UB3LYP distance, $r(\text{O}–\text{O}) = 2.22 \text{ \AA}$. In both instances, and with BLYP, $r(\text{O}–\text{O}) = 1.85$, the O–O bonds are significantly longer than what one might expect for a usual peroxide O–O bond length. Indeed, the experimental O–O distance in methyl hydroperoxide ($\text{CH}_3–\text{O}–\text{O}–\text{H}$)⁵⁵ is 1.47 \AA and the B3LYP/DZP O–O distance in the hydroperoxyethyl radical⁵⁶ is 1.45 \AA . To ensure that RB3LYP, UB3LYP, RBLYP, and UBLYP give correct results for peroxides, geometry optimizations of ordinary hydrogen peroxide were performed. These predict O–O bond lengths of 1.45 and 1.49 \AA for B3LYP and BLYP, respectively, with the unrestricted and restricted results being identical for both functionals. This is in good agreement with experimental distances of $\sim 1.47 \text{ \AA}$.^{57–59} The long O–O bond distances of hydroperoxycarbene and hydroperoxymethylcarbene suggest they may not be stable molecules but loosely bound complexes. In contrast, the respective O–O bond lengths for hydroperoxysilylene and hydroperoxymethylsilylene are 1.47 and 1.48 \AA for B3LYP and 1.54 and 1.56 \AA for BLYP with identical results for the restricted and unrestricted formalisms. These distances are similar to an O–O distance of 1.49 \AA computed with MP2/6-31G(d)¹⁴ and ensure us that a restricted wave function is valid for describing the remaining hydroperoxy systems of interest.

Geometries. The lowest energy conformations of formic acid, hydroperoxycarbene, acetic acid, and hydroperoxymethylcarbene (Figures 1–4) were used as the starting points for optimizing the geometry of the silicon, germanium, tin, and lead analogues of these species. For the other group 14 congeners of the hydroperoxymethylcarbene species, the minimum was of C_s symmetry rather than C_1 symmetry. Note that the lead congener

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of hydroperoxymethylcarbene has a small imaginary frequency, which corresponds to methyl rotation, with the BLYP functional only.

Optimized geometric parameters for the carbon, silicon, germanium, tin, and lead species at the various levels of theory employed are given in Supporting Information; however, we note here a few general trends and list in Figures 1–4 the BLYP/TZ2P ($X = C$) and BLYP/TZ2P-ECP ($X = Si, Ge, Sn, Pb$) geometries. Independent of basis set and molecule, BLYP usually predicts longer bond distances than B3LYP, in most cases by 0.01–0.02 Å.

In the formic acid congeners (Figure 1), the $X = C$ species (formic acid) has shorter bond lengths with the TZ2P basis over the DZP basis. However, examining the $X-O$ bond lengths (r_2 and r_3) in particular, we note that the TZ2P and/or TZ2P-ECP basis sets have almost no effect over DZP and/or DZP-ECP basis sets for $X = Si$ but show an increase in length for $X = Ge, Sn, and Pb$. For the silicon- and germanium-containing species, we can compare the all-electron DZP and TZ2P basis sets to the DZP-ECP and TZ2P-ECP basis sets. Here we note a considerable increase in $Si-O$ bond lengths for the ECP basis sets over the all-electron basis sets. However, the situation is reversed with $Ge-O$, where ECP basis sets now predict the shorter bond lengths.

As might be expected, all bond distances, except the $O-H$ length (r_1) increase steadily as one descends group 14. For example, BLYP/TZ2P-ECP results show that the $X-OH$ length (r_2) increases from about 1.4 to 2.0 Å. The $X=O$ double bond (r_3) is ~ 0.15 Å shorter than the $X-OH$ single bond (r_2) in all congeners. Kapp, Remko, and Schleyer have likewise noted that $X=O$ bonds are about 0.11–0.17 Å shorter than $X-O$ single bonds.⁵ The bond angles about X (θ_2 and θ_3) change only a few degrees between each congener, with the exception of $X = Pb$, where θ_2 is $\sim 7^\circ$ smaller than that in the $X = Sn$ congener and θ_3 is nearly 11° larger. Traditionally, such an effect would be interpreted as due to the inert pair effect,⁶⁰ which is thought to be most pronounced between Si and Pb .⁶¹ However, faults in the inert pair effect were noticed⁶² as early as 1958 and recent analysis by Kaupp and Schleyer emphasizes the differences in the sizes (radial extensions) of the s and p orbitals of Pb over Sn .⁹ Furthermore, Schwerdtfeger et al. noted that the ligand type also plays a significant role.⁴³

In the hydroperoxycarbene congeners (Figure 2), we see many of the same basis set and DFT functional trends as in the formic acid congeners. We observe a steady increase in the $X-O$ single bond (r_3) from 1.2 to 2.1 Å and note that this bond is slightly longer than the double bond in the formic acid congeners. Again, we emphasize that while the $O-O$ bond (r_2) in hydroperoxycarbene ($X = C$) is abnormally long, all other congeners show $O-O$ bond lengths close to what one might expect for hydrogen peroxide (~ 1.47 Å). It is interesting to note that the $H-X-O$ angle (θ_3) about the divalent group 14 atom is large for $X = C$ (127 degrees and consistent with sp^2 hybridization) but more acute for all other group 14 atoms (~ 97 degrees). Kutzelnigg has noted that “*hybridization defects*” in heavier group 14 atoms cause the orthogonal hybrids usually seen in carbon to be substantially distorted.^{63,64} These hybridization defects are consistent with the acute $H-X-O$ angle in the heavy-element

congeners of hydroperoxycarbene. It should be noted that the small divalent angles for $X = Si, Ge, Sn, and Pb$ have been seen before in other divalent group 14 molecules.^{5,9,63}

The geometric trends in both the acetic acid and hydroperoxymethylcarbene congeners (Figures 3 and 4) are quite similar to those of the formic acid and hydroperoxycarbene congeners. Again, we emphasize that while the $O-O$ bond distance (r_2) in hydroperoxymethylcarbene is abnormally large for $X = C$ (~ 2.0 Å), all other congeners have distances of ~ 1.5 Å. It is also interesting to note that the divalent hybridization angle, $C-X-O$ (θ_3 in Figure 4) is slightly larger than the corresponding angle in the hydroperoxycarbene congeners. This is likely due to the presence of the methyl substituent.

Bonding. (1) NBO Analysis. In their analysis of group 14 formaldehyde congeners, Kapp et al. represented the ionic $X=O$ double bond as $^-O::X^+$, which emphasizes the largely polar character of both the σ and π bonds.⁵ In support of this characterization, Kapp et al. used B3LYP NBO analysis. Our B3LYP/DZP and B3LYP/DZP-ECP NBO analysis (Table 1) of the $X=O$ double bonds in the formic acid congeners shows that these double bonds are very similar to those of the formaldehyde congeners. For example, Kapp et al. showed a small positive natural atomic charge (NAC) for the C atom in formaldehyde (0.29) but larger NACs on the subsequent group 14 atoms (1.49–1.71). Our NACs in formic acid likewise show that the C atom has a relatively small NAC (0.72) with larger NACs on the other group 14 atoms (1.76–2.01). In fact, both the doubly bonded oxygen and the singly bonded OH oxygen atom have large negative NACs (around -1.0), suggesting that both the oxygen single and oxygen double bonds in the $Si-, Ge-, Sn-, and Pb-$ substituted formic acid congeners are highly polar.

A nonpolar natural population analysis (NPA) double bond has a bond order of 2.0. For the highly polar $^-O::X^+$ bonds of the formaldehyde congeners, Kapp et al. obtained NPA bond orders of 1.4 for $^-O::C^+$ and 0.84–0.91 for the $^-O::X^+$ ($X = Si, Ge, Sn, Pb$) double bonds. Our computed NPA bond orders for the $^-O::X^+$ bonds of the formic acid congeners are very similar to those reported by Kapp et al. Note that the $X-OH$ single bonds show a bond order of approximately half those of the $^-O::X^+$ bonds, suggesting, as one would expect, that these are indeed polarized single bonds.

The hydroperoxycarbene congeners for $X = Si, Ge, Sn, and Pb$ show similar bond orders for the metal oxygen $X-OOH$ single bonds. However, the $C-O$ bond in hydroperoxycarbene has a bond order of 1.69, which is even greater than the $^-O::C^+$ bond order in formic acid and suggestive of a double bond. It appears that hydroperoxycarbene is a loose complex between the hydroxyl radical and HCO (see earlier discussion). Examining the $O-O$ peroxy bond of hydrogen peroxide, we see that the nonpolar $O-O$ single bond order is exactly 1.0. Likewise, the bond orders of the $O-O$ bonds in the $X = Si, Ge, Sn, Pb$ congeners are of nearly 1.0, suggesting the $O-O$ bond in these divalent species is very similar to that of hydrogen peroxide. In contrast, the $O-O$ bond order in hydroperoxycarbene is very small (0.31), suggesting a rather weakly bound complex. Recall also that the $O-O$ bonds lengths of the $X = Si, Ge, Sn, Pb$ congeners were similar to that of hydrogen peroxide, but the $O-O$ bond length in hydroperoxycarbene is significantly longer. Finally, it should be noted that the use of the ECP for Si and Ge made very little difference on the bonding characteristics of the NBO analysis in comparison to the all-electron DZP NBO results.

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Table 1. Natural Atomic Charges (NAC) and Bond Orders (NPA) from the B3LYP/DZP and B3LYP/DZP-ECP Natural Bond Order Analysis for the Formic Acid and Hydroperoxycarbene Congeners

| | Acids | | | | | | | |
|--------|----------------|------|----------------|------|------|------|------|------|
| | NAC | | | | NPA | | | |
| | O ^a | X | O ^b | H | X=O | X-OH | O-H | X-H |
| C | -0.62 | 0.72 | -0.74 | 0.51 | 1.31 | 0.72 | 0.47 | 0.80 |
| Si | -1.11 | 1.93 | -1.10 | 0.54 | 0.85 | 0.41 | 0.46 | 0.74 |
| Si/ECP | -1.10 | 1.92 | -1.10 | 0.53 | 0.85 | 0.40 | 0.46 | 0.74 |
| Ge | -1.03 | 1.76 | -1.06 | 0.52 | 0.93 | 0.43 | 0.47 | 0.79 |
| Ge/ECP | -1.07 | 1.88 | -1.10 | 0.53 | 0.88 | 0.40 | 0.47 | 0.75 |
| Sn/ECP | -1.09 | 2.01 | -1.14 | 0.52 | 0.87 | 0.35 | 0.48 | 0.69 |
| Pb/ECP | -1.01 | 1.85 | -1.11 | 0.50 | 0.94 | 0.37 | 0.49 | 0.72 |

| | Hydroperoxides | | | | | | | |
|-------------------------------|----------------|-------|-------|------|-------|------|------|------|
| | NAC | | | | NPA | | | |
| | X | O | O | H | X-OOH | O-O | O-H | X-H |
| C | 0.35 | -0.30 | -0.68 | 0.46 | 1.69 | 0.31 | 0.54 | 0.76 |
| Si | 0.95 | -0.66 | -0.46 | 0.49 | 0.45 | 0.91 | 0.50 | 0.66 |
| Si/ECP | 0.93 | -0.65 | -0.46 | 0.49 | 0.45 | 0.91 | 0.50 | 0.67 |
| Ge | 0.96 | -0.64 | -0.46 | 0.48 | 0.42 | 0.94 | 0.50 | 0.64 |
| Ge/ECP | 0.90 | -0.62 | -0.46 | 0.48 | 0.43 | 0.94 | 0.50 | 0.68 |
| Sn/ECP | 1.07 | -0.67 | -0.47 | 0.48 | 0.36 | 0.96 | 0.51 | 0.58 |
| Pb/ECP | 1.06 | -0.65 | -0.48 | 0.48 | 0.36 | 0.98 | 0.51 | 0.58 |
| H ₂ O ₂ | - | - | -0.48 | 0.48 | - | 1.00 | 0.51 | - |

^a Double-bonded oxygen (X=O). ^b Single-bonded oxygen (X-O-H).

Table 2. Bond Energies (in kcal/mol) for the X=O Double Bond of the Formic Acid Congeners and the O-O Peroxy Bond in Hydroperoxycarbene Congeners^a

| X | X=O ^b | X=O ^c | XO-OH ^d | ΔE | |
|----|------------------|------------------|--------------------------|--------------------------|-----------|
| | | | | bonds | molecules |
| C | 200.8 | 255.7 | 13.9 | 186.9 | 99.4 |
| Si | 150.8 | 190.5 | 25.7 | 125.1 | 84.7 |
| Ge | 123.5 | 156.4 | 35.7 | 87.8 | 58.9 |
| Sn | 105.0 | 126.6 | 43.4 (40.2) ^e | 61.6 (64.8) ^e | 41.6 |
| Pb | 79.7 | 88.3 | 49.2 (37.8) ^f | 30.5 (41.9) ^f | 16.0 |

^a Also shown are the experimental dissociation energies for the group 14 monoxides (X=O). All energies are with BLYP/DZP-ECP, except X = C, which is with BLYP/DZP. ^b Computed as $\Delta E \{H(X=O)OH (^1A') - cis H-X-O-H (^1A') - O (^1D)\}$. ^c Experimental dissociation energy for the isolated diatomic molecule. See ref 65. ^d Computed as $\Delta E \{H-X-O-OH (^1A') - H-X-O (^2A') - OH (^2\Pi)\}$. ^e Estimated value including spin-orbit effects of HSnO. Estimated from the spin-orbit coupling in isoelectronic SbO: $\Delta E(^2\Pi_{3/2} - ^2\Pi_{1/2})/2 \approx 3.2$ kcal/mol. See ref 65. ^f Estimated value including spin-orbit effects of HPbO. Estimated from the spin-orbit coupling in isoelectronic BiO: $\Delta E(^2\Pi_{3/2} - ^2\Pi_{1/2})/2 \approx 11.4$ kcal/mol. See ref 65.

(2) Bond Strengths. One explanation for the stability of the tetravalent formic acid congeners over their isomeric divalent hydroperoxycarbene congeners (See Tables 3 and 4 and the section on Relative Energies below) would be the relative bond strengths of the $\text{O}::\text{X}^+$ double bonds over the O-O peroxy-like bonds. Table 2 shows the relative strengths of the $\text{O}::\text{X}^+$ double bonds and the O-O peroxy-like bonds. The bond energies are at the BLYP/DZP level and were determined simply from differences in absolute energies and are without zero-point correction. The O-O bond in hydroperoxycarbene is very weak, 14 kcal/mol, and consistent with the NPA bond order of ~ 0.3 . Interestingly, the O-O bond strength increases by ~ 10 kcal/mol for Si and again for Ge. The increase in O-O bond energies is accompanied by a corresponding decrease in $\text{O}::\text{X}^+$ double bond energies in the formic acid congeners from 201 kcal/mol for carbon to only 80 kcal/mol for lead. This decrease in metal-oxygen bond strengths is not unexpected, as the diatomic metal monoxides (XO) also show a large decrease in their dissociation

energies.⁶⁵ Taking the difference in the two bond energies, we see that the double bond is strongly preferred by carbon (by 187 kcal/mol) but much less preferred by lead (only 42 kcal/mol). Clearly the strong $\text{O}::\text{X}^+$ double bond is the major explanation for the preferred tetravalency of the group 14 acids, and its weakening with heavier group 14 elements, along with an increasingly more stable O-O bond allows the divalent hydroperoxycarbene congeners to become relatively more stable.

Relative Energies. Tables 3 and 4 show the energies of formic and acetic acid congeners relative to their hydroperoxy isomers. Almost without exception, increasing the basis set from a DZP or DZP/ECP basis to a TZ2P or TZ2P/ECP basis increases the stability of the tetravalent acid congener. CCSD and CCSD(T) single-point energies further favor tetravalency, such that our best results, CCSD(T)/TZ2P//BLYP/TZ2P and CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP, are about 4–13 kcal/mol more in favor of tetravalency than BLYP/TZ2P or BLYP/TZ2P-ECP. The BLYP relative energies are substantially lower than the B3LYP energies for X = C and X = Si but are very similar to or even slightly higher for X = Ge, Sn, and Pb. It is clear that hydroperoxycarbene and hydroperoxymethylcarbene are much less stable (more than 100 kcal/mol) than their parent acids, in good agreement with a loosely bound complex for these carbene species. The relative energies for the two silicon hydroperoxy compounds are likewise more than 100 kcal/mol above their acid isomers. In fact, the CCSD(T)/TZ2P//BLYP/TZ2P value of 110.4 kcal/mol for HSiOOH relative to H(Si=O)OH is in excellent agreement with the G2 value of 110.3 kcal/mol.¹⁴ Note, however, that the bonding analysis and geometries of the two silicon hydroperoxides suggest they are truly bound, despite their relatively high energies. Although a significant increase in the relative stability of the hydroperoxycarbene congeners is observed for X = Ge, Sn, and Pb as compared to X = C and Si, even lead favors tetravalency by ~ 25 kcal/mol.

In contrast to the H₂XO species where the divalent carbene-like H \ddot{X} OH species are favored in all cases except X = C,⁵

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Table 3. Energies (in kcal/mol) of the Group 14 Hydroperoxide Compounds ($\text{H}\ddot{\text{X}}\text{OOH}$ (**2**) and $\text{CH}_3\ddot{\text{X}}\text{OOH}$ (**4**)) Relative to Their Corresponding Acid Isomers ($\text{H}(\text{X}=\text{O})\text{OH}$ (**1**) and $\text{CH}_3(\text{X}=\text{O})\text{OH}$ (**3**)) for the B3LYP, BLYP, CCSD, and CCSD(T) Methods Using the DZP and TZ2P Basis Sets (See Figures 1–4)

| method and basis | X = C | | X = Si | | X = Ge | |
|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | $\Delta E(2-1)$ | $\Delta E(4-3)$ | $\Delta E(2-1)$ | $\Delta E(4-3)$ | $\Delta E(2-1)$ | $\Delta E(4-3)$ |
| B3LYP/DZP | 113.3 | 107.2 | 102.0 | 103.7 | 58.2 | 60.4 |
| BLYP/DZP | 99.4 | 92.4 | 96.5 | 97.6 | 55.3 | 57.2 |
| B3LYP/TZ2P | 111.0 | 103.2 | 107.1 | 108.8 | 60.2 | 62.2 |
| BLYP/TZ2P | 96.4 | 88.1 | 101.0 | 101.9 | 57.0 | 58.7 |
| CCSD/TZ2P//BLYP/TZ2P | 117.6 | 112.9 | 112.3 | 115.7 | 67.1 | 69.2 |
| CCSD(T)/TZ2P//BLYP/TZ2P | 105.4 | 100.0 | 110.4 | 112.9 | 67.8 | 69.6 |

Table 4. Energies (in kcal/mol) of the Group 14 Hydroperoxide Compounds ($\text{H}\ddot{\text{X}}\text{OOH}$ (**2**) and $\text{CH}_3\ddot{\text{X}}\text{OOH}$ (**4**)) Relative to Their Corresponding Acid Isomers ($\text{H}(\text{X}=\text{O})\text{OH}$ (**1**) and $\text{CH}_3(\text{X}=\text{O})\text{OH}$ (**3**)) for the B3LYP, BLYP, CCSD, and CCSD(T) Methods Using the DZP-ECP and TZ2P-ECP Basis Sets (See Figures 1–4)

| method and basis | X = Si | | X = Ge | | X = Sn | | X = Pb | |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | $\Delta E(2-1)$ | $\Delta E(4-3)$ | $\Delta E(2-1)$ | $\Delta E(4-3)$ | $\Delta E(2-1)$ | $\Delta E(4-3)$ | $\Delta E(2-1)$ | $\Delta E(4-3)$ |
| B3LYP/DZP-ECP | 88.4 | 89.7 | 60.0 | 63.1 | 40.3 | 43.7 | 12.8 | 17.0 |
| BLYP/DZP-ECP | 84.7 | 85.4 | 58.9 | 61.6 | 41.6 | 45.0 | 16.0 | 20.4 |
| B3LYP/TZ2P-ECP | 96.9 | 99.0 | 67.5 | 69.8 | 47.8 | 50.0 | 19.5 | 22.5 |
| BLYP/TZ2P-ECP | 92.1 | 93.1 | 65.5 | 67.2 | 48.4 | 50.4 | 22.1 | 25.1 |
| CCSD/TZ2P-ECP//BLYP/TZ2P-ECP | 106.2 | 108.9 | 75.5 | 77.1 | 54.6 | 55.9 | 24.3 | 26.2 |
| CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP | 104.7 | 106.4 | 75.8 | 77.0 | 56.3 | 57.3 | 26.8 | 28.9 |

tetravalent formic acid is clearly favored over its carbene-like isomer for each group 14 congener. Kapp et al. observed that methyl substitution (Me_2XO vs H_2XO) stabilizes the double bond isomer.⁵ We note a similar trend in all cases (except $\text{X}=\text{C}$): acetic acid congeners are more stable relative to their hydroperoxymethylcarbene congeners than the formic acid congeners are to the hydroperoxycarbene congeners. However, this stabilization is not more than a few kilocalorie per mole. On the other hand, noting that Kaupp and Schleyer have shown that electronegative substituents destabilize tetravalent Pb compounds,⁹ perhaps FPbOOH compounds may favor tetravalency by less than 20 kcal/mol.

Finally, we note that the ECP basis sets give lower relative energies than the all-electron basis for Si but higher relative energies for Ge. It is not clear what factors may cause these discrepancies. Nonetheless, it is reasonable to assume that the results presented in Tables 3 and 4 are accurate to within 10 kcal/mol. For example, we expect the tetravalent formic acid-like Pb congener to be 26.8 ± 10.0 kcal/mol more stable than its divalent carbene-like isomer.

Conclusions

The relative stabilities of tetravalent group 14 formic acid and acetic acid congeners over their divalent hydroperoxycarbene and hydroperoxymethylcarbene isomers have been determined using the B3LYP and BLYP density functionals and the CCSD and CCSD(T) ab initio methods. In all cases, the tetravalent isomer is preferred, though the relative stability of the carbene-like isomer increases as one descends group 14. The methyl substituent in acetic acid slightly stabilizes acetic acid over formic acid.

The metal–oxygen double bond $\text{O}::\text{X}^+$ of the acid congeners is seen to be highly polar, as previously observed in the

formaldehyde series,⁵ and its bond strength drops considerably as one descends group 14. In contrast, the O–O peroxy bond of the hydroperoxy carbene-like species is increasingly stabilized by heavier group 14 elements, such that the divalent $\text{H}-\ddot{\text{Pb}}-\text{O}-\text{O}-\text{H}$ and $\text{Me}-\ddot{\text{Pb}}-\text{O}-\text{O}-\text{H}$ species are only 27 and 29 kcal/mol less stable than their acid isomers.

It is interesting to note that these results are in contrast to those of H_2XO , where the divalent carbene-like isomers of this series are the most stable (by nearly 70 kcal/mol for Pb).⁵ Clearly, more studies on the tetravalent/divalent character of group 14 atoms are of interest.

Because of their high relative energy, the hydroperoxycarbene and hydroperoxymethylcarbene congeners of carbon and silicon would be difficult to isolate under most experimental conditions. However, the analogous germanium, tin, and lead carbene congeners may be detectable in a low-temperature matrix isolation experiment, as they are much more stable. Furthermore, because both formic and silanoic acid have been characterized spectroscopically, the germanium, tin, and lead formic and acetic acid-like species, which are more stable than their carbene isomers, appear to be suitable candidates for spectroscopic investigation.

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Supporting Information Available: Tables of optimized molecular geometries for all species with the B3LYP and BLYP functionals and the DZP, DZP-ECP, TZ2P, and TZ2P-ECP basis sets (Tables 5–8) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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