

Examination of the Stabilities of Group 14 (C, Si, Ge, Sn, Pb) Congeners of Dihydroxycarbene and Dioxirane. Comparison to Formic Acid and Hydroperoxycarbene Congeners

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The relative energetics of four XH_2O_2 ($\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) isomers, dihydroxycarbene, formic acid, dioxirane, and hydroperoxycarbene, were determined using the BLYP and B3LYP density functionals with DZP and TZ2P basis sets, as well as CCSD and CCSD(T) single-point energies at the BLYP/TZ2P optimized geometries. Relative to dihydroxycarbene, formic acid was 41.8 kcal/mol lower in energy while dioxirane and hydroperoxycarbene were 51.3 and 63.6 kcal/mol higher, respectively, with CCSD(T). Furthermore, using an effective core potential (ECP) the dihydroxy congener was shown to be the most stable isomer for $\text{X} = \text{Si}-\text{Pb}$. The formic acid and dioxirane congeners become increasingly less stable as one descends group 14. Our results show that divalency is preferred for Si–Pb (dihydroxy congeners are the most stable) but the tetravalent formic acid congeners remain more stable than the hydroperoxy congeners, showing that divalency is not universally preferred among these isomers.

1. Introduction

Examination of the relative energies among isomers of a series of congeners provides insight into bonding trends in a periodic group. In recent work Kapp, Remko, and Schleyer found that the relative energies for XH_2O molecules of group 14 congeners were lower for the divalent $\text{H}-\ddot{\text{X}}-\text{O}-\text{H}$ isomers than for the tetravalent $\text{H}_2\text{X}=\text{O}$ isomers in all species except $\text{X} = \text{C}$. For $\text{X} = \text{Si}$ the difference was only about 2 kcal/mol but increased to about 70 kcal/mol for $\text{X} = \text{Pb}$. In contrast, the carbon congener $\text{H}_2\text{C}=\text{O}$ (formaldehyde) was about 58 kcal/mol more stable than $\text{H}-\ddot{\text{C}}-\text{O}-\text{H}$ (hydroxymethylene).¹ Other work by Martin indicates the tetravalent silicon isomer ($\text{H}_2\text{Si}=\text{O}$) is about 0.5 kcal/mol more stable than the divalent silicon isomer ($\text{H}-\ddot{\text{Si}}-\text{O}-\text{H}$);² nonetheless, the two are still quite close in energy. Kapp, Remko, and Schleyer's work is in accord with the empirical notion that heavier group 14 atoms prefer divalent bonding. For example, using the CCSD(T)/TZ2P method Heinemann, Herrmann, and Thiel found aminosilylenes and aminogermynes to be thermodynamically stable with respect to their tetravalent isomers, a result in contrast to that for the analogous aminocarbenes.³ This preference for divalency over tetravalency should depend on the bonding characteristics of particular ligand groups attached to the central metal atom.

Indeed, stable carbenes are difficult to obtain without stabilization through aromaticity or steric hindrance through bulky substituents.⁴ Furthermore, Hitchcock and co-workers examined divalent cyclic carbenes, silylenes, germynes, and

their analogous tetravalent species and noted that the divalent center in carbenes is qualitatively different than that in silylenes or germynes.^{5,6} Other work by Kaupp and Schleyer found that the electronegative substituents F and Cl destabilize tetravalent lead compounds.⁷ Yet recent work by Seth, Faegri, and Schwerdtfeger indicate that tetravalent PbX_4 compounds are more stable toward decomposition into $\text{PbX}_2 + \text{X}_2$ with $\text{X} = \text{Cl}$ or F than with $\text{X} = \text{H}$.⁸ Thus, it is still unclear how one rationalizes and predicts stability differences and trends between tetravalent and divalent isomers of group 14 compounds.

Previously we studied relative energies for the group 14 congeners of hydroperoxycarbene ($\text{H}-\ddot{\text{X}}-\text{O}-\text{O}-\text{H}$) and formic acid ($\text{HX}(\text{=O})\text{OH}$).⁹ Tetravalency was preferred by all group 14 atoms, but the preference over divalency decreased from 105 kcal/mol for $\text{X} = \text{C}$ to only 27 kcal/mol for $\text{X} = \text{Pb}$. The increase in stabilization of hydroperoxycarbene relative to formic acid was explained by the stabilization of the peroxy $\text{O}-\text{O}$ bond by heavier group 14 atoms and the destabilization of the $\text{X}=\text{O}$ double bond in the formic acid congeners. Nonetheless, the preference for tetravalency was in contrast to the $\text{H}_2\text{X}=\text{O}$ vs HXOH results of Schleyer et al.,¹ where divalency was preferred for all species except $\text{X} = \text{C}$.

This present work investigates the congeners of two new XH_2O_2 isomers: dihydroxycarbene ($\ddot{\text{X}}(\text{OH})_2$) and dioxirane (XH_2OO). Both carbon congeners of these molecules have been studied experimentally and theoretically. Burgers, McGibbon, and Terlouw generated and identified dihydroxycarbene $\text{HO}-\ddot{\text{C}}-\text{OH}$ in the gas phase by electron capture in neutralization–

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reionization experiments.¹⁰ Theoretical work has studied the singlet and triplet states of dihydroxycarbene,^{11,12} as well as its role as an intermediate in the dissociation of formic acid.^{13,14} The dioxirane isomer was studied experimentally in work by Lovas and Suenram who used microwave spectroscopy in the first identification of dioxirane, found as an intermediate in the low-temperature reaction between ozone and ethylene.^{15,16} Martinez, Huie, and Herron confirmed this finding using low-temperature techniques, which allowed characterization by photoionization mass spectrometry.¹⁷ Recent theoretical studies have also predicted the structure and frequencies of dioxirane^{18–22} as well as some substituted dioxiranes.^{23,24} Other theoretical studies examined and compared dioxirane to the less stable isomer, carbonyl oxide ($\text{H}_2\text{X}-\text{O}-\text{O}$).^{25–29}

The decomposition of carbonyl oxide produced from oxidation of methylene has been proposed to proceed either through dioxirane which rearranges to formic acid or through hydroperoxycarbene which dissociates to form OH and HCO radicals.^{30,31} Although reactions of carbonyl oxide are experimentally important,^{32,33} we have chosen not to include carbonyl oxide in the present work since at the CCSD(T) level with a TZ2P basis it is shown to be 26 kcal/mol less stable than dioxirane.²⁷ Furthermore, its bonding displays trivalency and our work primarily compares tetravalency and divalency.

Previous work has also explored the silicon congeners of dihydroxide, dioxirane, and carbonyl oxide.^{34–42} One experi-

mental study of silylene–oxygen adducts observed the silicon congener of carbonyl oxide ($\text{H}_2\text{Si}-\text{O}-\text{O}$) in a matrix IR spectrum but not the dioxirane congener.³⁵ Theoretical work, however, argues that $\text{H}_2\text{Si}-\text{O}-\text{O}$ is kinetically unstable and rapidly cyclizes to H_2SiO_2 .³⁷ Using G2 theory, Darling and Schlegel predicted the silicon congener of carbonyl oxide to be 63 kcal/mol higher in energy than siladioxirane.³⁸ Other theoretical work arrived at a similar prediction for this relative stability.³⁹ The other silicon congeners as well as related compounds of silicon, oxygen, and hydrogen have also been studied as possible intermediates in silane combustion.^{38,40–43}

Little is known about the germanium, tin, and lead XH_2O_2 congeners. The germanium congener of dihydroxycarbene has been studied in the solid phase⁴⁴ but to our knowledge not in the gas phase. One theoretical work did examine $\text{Sn}(\text{OH})_2$ in the redox reaction of $\text{Sn}(\text{OH})_2$ to $\text{Sn}(\text{OH})_4$.⁴⁵ Although $\text{Sn}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$ are pervasive in many areas of chemistry as insoluble precipitates, to our knowledge neither has been examined experimentally in the gas phase via spectroscopy or theoretically by ab initio methods. Furthermore, the dioxiranes of Ge, Sn, and Pb are at present unknown.

Since the divalent isomers with electronegative substituents bonded to at least one side of the central metal atom appear to be more stable as one descends group 14,^{1,7,9} especially for the –OH substituent,^{1,9} we might expect the dihydroxycarbene congeners to be quite stable, particularly those of the heavier members of group 14. We investigate this possibility in the present work by comparing relative energies of the group 14 congeners of dihydroxycarbene [$\text{H}-\text{O}-\ddot{\text{C}}-\text{O}-\text{H}$], formic acid [$\text{HC}(=\text{O})\text{OH}$], dioxirane [CH_2OO], and hydroperoxycarbene [$\text{H}-\ddot{\text{C}}-\text{O}-\text{O}-\text{H}$], all isomers of XH_2O_2 . Analysis of bonding and dissociation energies provides some explanations for the trends observed.

2. Theoretical Methods

In order to directly compare our current results for the dihydroxycarbene and dioxirane congeners to those of formic acid and hydroperoxycarbene from our previous study,⁹ we have used methods identical to those of our previous work. 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)⁴⁶ in conjunction with one of Becke's exchange functionals: the 3-parameter HF/DFT hybrid exchange functional (B3)⁴⁷ for B3LYP or the pure DFT exchange functional (B)⁴⁸ for BLYP. The Gaussian94 system of programs⁴⁹ was used. The OPT=TIGHT parameter was used in geometry optimizations. The coupled cluster

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with single and double excitations (CCSD) method^{50–52} and the CCSD with perturbative triple excitations CCSD(T) method^{53,54} were used to generate single-point energies at BLYP/TZ2P and BLYP/TZ2P-ECP optimized geometries. The ACES II program⁵⁵ was employed for the coupled cluster results.

To ensure that all species were minima, harmonic vibrational frequencies were determined at the DZP and/or DZP-ECP level of theory for both B3LYP and BLYP. Harmonic frequencies were computed analytically for the all-electron basis set (DZP) and via finite differences of analytic first derivatives for effective core potential 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^{56,57} 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 [$\alpha_p(\text{H}) = 0.75$, $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{O}) = 0.85$, $\alpha_d(\text{Si}) = 0.50$] for each C, O, and Si atom. We also employed the triple- ζ Gaussian basis of Dunning^{58,59} augmented with two sets of p polarization functions for each H atom and two sets of five d polarization functions [$\alpha_p(\text{H}) = 1.50$, $\alpha_d(\text{C}) = 1.50$, $\alpha_d(\text{O}) = 1.70$, $\alpha_d(\text{Si}) = 1.00$, 0.25] for each C, O, and Si atom. For Ge the triple- ζ basis set of Dunning⁶⁰ augmented with one set of five d polarization functions, where $\alpha_d(\text{Ge}) = 0.25$, 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 effective core potential (ECP) as given by the LANL2DZ basis set.^{61–63} 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, as d valence participation is expected to be small in these molecules.¹ Molecular spin-orbit effects were not considered and are expected to be small for closed-shell species.^{64–67}

Finally, it should be noted that the B3 exchange functional is a parametrized functional and has been fit only to first- and second-row

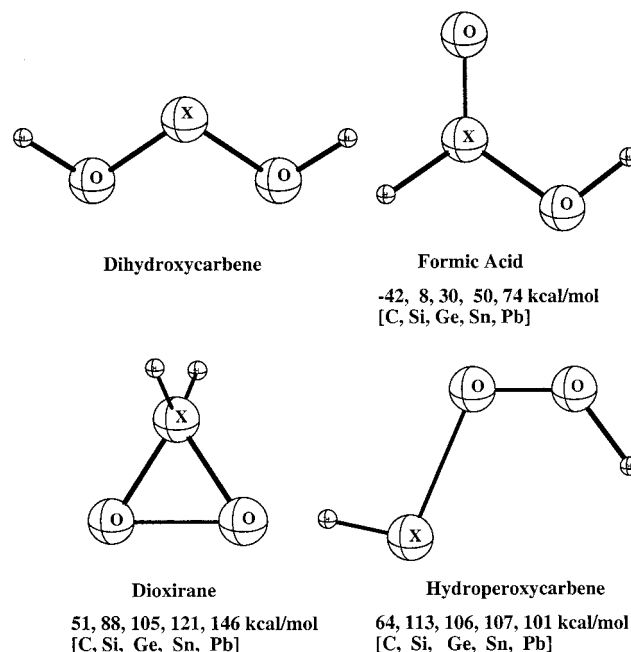


Figure 1. Four isomers of XH_2O_2 , where $\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$. Relative energies with respect to the dihydroxycarbene congener are given; CCSD(T)/TZ2P//BLYP/TZ2P used for $\text{X} = \text{C}$, and CCSD(T)/TZ2P//BLYP/TZ2P-ECP used for $\text{X} = \text{Si–Pb}$.

compounds.⁴⁷ Thus we may 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 natural bond order (NBO) analysis of Reed and Weinhold.^{68–71} Analysis was done at the B3LYP/DZP and B3LYP/DZP-ECP levels.

3. Results and Discussion

Full geometry optimizations of dihydroxycarbene and dioxirane congeners gave minima with all real harmonic frequencies in every case. Figure 1 displays the conformations of all the isomers studied. All dihydroxycarbene and dioxirane congeners have C_{2v} symmetry and $^1\text{A}_1$ ground states. Figure 1 shows the trans–trans conformation of dihydroxycarbene. Another conformation of dihydroxycarbene results from the rotation of one O–H bond about the O–X bond to produce a cis–trans geometry. With B3LYP/DZP the trans–trans conformation is 0.18 kcal/mol lower than the cis–trans for the carbon congener. For silicon and germanium the cis–trans conformations are 2.27 and 2.78 kcal/mol lower, respectively, than the trans–trans, likely because the smaller O–X–O angle allows for a favorable $\text{H–O}\cdots\text{H–O}$ interaction. However, for uniform comparison to the carbon congener, all other results were obtained using the trans–trans conformation of the dihydroxycarbene congeners. All formic acid and hydroperoxycarbene results were taken directly from our previous work.⁹

3.1. Geometries. Tables 1 and 2 report the optimized geometric parameters corresponding to Figures 2 and 3 for the carbon, silicon, germanium, tin, and lead congeners of dihydroxycarbene and dioxirane at the various levels of theory

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Table 1. Comparison of the Optimized Geometric Parameters for the Group 14 Congeners of the Dihydroxycarbene Molecule Represented in Figure 2 (Bond Lengths, Å, Angles, deg)

	method/basis	X = C	X = Si	X = Ge	X = Sn	X = Pb
r_1	B3LYP/DZP	1.338	1.662	1.795		
r_1	BLYP/DZP	1.359	1.683	1.822		
r_1	B3LYP/DZP-ECP		1.678	1.787	1.934	2.009
r_1	BLYP/DZP-ECP		1.699	1.810	1.956	2.034
r_1	B3LYP/TZ2P	1.327	1.661	1.803		
r_1	BLYP/TZ2P	1.347	1.683	1.831		
r_1	B3LYP/TZ2P-ECP		1.675	1.787	1.941	2.016
r_1	BLYP/TZ2P-ECP		1.697	1.811	1.964	2.041
r_2	B3LYP/DZP	0.970	0.968	0.970		
r_2	BLYP/DZP	0.980	0.978	0.981		
r_2	B3LYP/DZP-ECP		0.968	0.968	0.967	0.968
r_2	BLYP/DZP-ECP		0.979	0.979	0.978	0.979
r_2	B3LYP/TZ2P	0.963	0.960	0.962		
r_2	BLYP/TZ2P	0.973	0.970	0.972		
r_2	B3LYP/TZ2P-ECP		0.959	0.960	0.959	0.960
r_2	BLYP/TZ2P-ECP		0.970	0.970	0.969	0.970
θ_1	B3LYP/DZP	104.5	115.7	112.7		
θ_1	BLYP/DZP	103.8	114.5	111.3		
θ_1	B3LYP/DZP-ECP		115.5	115.2	119.4	117.9
θ_1	BLYP/DZP-ECP		114.1	113.7	117.5	115.9
θ_1	B3LYP/TZ2P	104.8	115.3	112.7		
θ_1	BLYP/TZ2P	104.2	114.3	111.4		
θ_1	B3LYP/TZ2P-ECP		114.3	113.8	117.3	116.1
θ_1	BLYP/TZ2P-ECP		113.3	112.6	115.8	114.5
θ_2	B3LYP/DZP	105.7	97.5	93.6		
θ_2	BLYP/DZP	104.7	97.0	93.1		
θ_2	B3LYP/DZP-ECP		95.9	93.0	91.4	90.8
θ_2	BLYP/DZP-ECP		95.4	92.5	90.8	90.2
θ_2	B3LYP/TZ2P	106.6	97.1	93.1		
θ_2	BLYP/TZ2P	105.7	96.7	92.8		
θ_2	B3LYP/TZ2P-ECP		96.1	93.4	91.8	91.2
θ_2	BLYP/TZ2P-ECP		95.6	93.1	91.4	90.9

employed. Independent of basis set and molecule, BLYP usually predicts longer bond distances than B3LYP, in most cases by 0.01–0.02 Å.

Overall, the effect of basis set and method on bond lengths and angles is slight in the dihydroxycarbene congeners (Table 1 and Figure 2). The geometry for the silicon congener approximately agrees with previous theoretical work. Using the MP2/6-31G(d) method Darling and Schlegel obtained $r_1 = 1.667$ Å, $r_2 = 0.972$ Å, $\theta_1 = 113.2^\circ$, and $\theta_2 = 97.4^\circ$.³⁸ Our B3LYP/TZ2P values were 1.661 Å, 0.960 Å, 115.3°, and 97.1°, respectively, for each parameter.

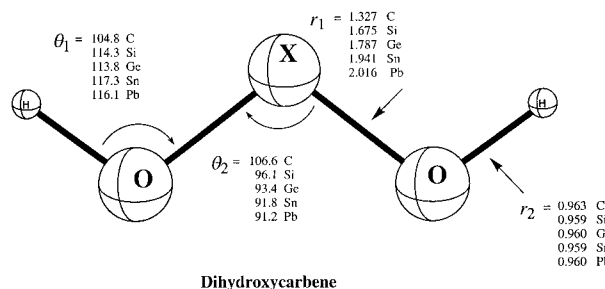
In the present results we see that X = C has shorter X–O (r_1) bond lengths with the TZ2P basis than with the DZP basis. However, for X = Si the DZP basis gives the same bond length as the TZ2P basis while for X = Ge the bond length is longer for the TZ2P basis than for the DZP basis. Note also that for X = Si the effect of the TZ2P-ECP basis over the DZP-ECP basis shortens the bond, but for X = Ge the bond length remains the same and, for X = Sn and Pb, the bond length increases. In every case the O–H bond (r_2) lengths shorten from the DZP and DZP-ECP basis to the TZ2P and TZ2P-ECP basis sets. The angles vary at most by about 2° among various basis sets and methods for all the congeners.

For the X–O bond (r_1) the change with the descent through group 14 is predictable: the bond lengthens. The O–H bond (r_2), which is not directly affected by the metal atom, shows little change between congeners.

The angles show the greatest variation between the carbon congeners and all others. The X–O–H angles (θ_1) increase from a nearly tetrahedral angle of 104–105° for X = C to around 114–115° for X = Si but then decrease approximately 2–3° from Si to Ge. Interestingly, a similar increase followed by a

Table 2. Comparison of the Optimized Geometric Parameters for the Group 14 Congeners of the Dioxirane Molecule Represented in Figure 3 (Bond Lengths, Å, Angles, deg)

	method/basis	X = C	X = Si	X = Ge	X = Sn	X = Pb
r_1	B3LYP/DZP	1.096	1.472	1.525		
r_1	BLYP/DZP	1.105	1.482	1.538		
r_1	B3LYP/DZP-ECP		1.455	1.522	1.688	1.709
r_1	BLYP/DZP-ECP		1.463	1.532	1.698	1.724
r_1	B3LYP/TZ2P	1.087	1.470	1.526		
r_1	BLYP/TZ2P	1.094	1.480	1.539		
r_1	B3LYP/TZ2P-ECP		1.466	1.529	1.696	1.718
r_1	BLYP/TZ2P-ECP		1.474	1.538	1.706	1.732
r_2	B3LYP/DZP	1.397	1.658	1.791		
r_2	BLYP/DZP	1.416	1.678	1.816		
r_2	B3LYP/DZP-ECP		1.688	1.785	1.936	2.001
r_2	BLYP/DZP-ECP		1.707	1.806	1.958	2.027
r_2	B3LYP/TZ2P	1.391	1.653	1.794		
r_2	BLYP/TZ2P	1.410	1.673	1.819		
r_2	B3LYP/TZ2P-ECP		1.678	1.778	1.931	1.992
r_2	BLYP/TZ2P-ECP		1.697	1.799	1.954	2.019
r_3	B3LYP/DZP	1.503	1.583	1.559		
r_3	BLYP/DZP	1.540	1.626	1.600		
r_3	B3LYP/DZP-ECP		1.558	1.555	1.550	1.544
r_3	BLYP/DZP-ECP		1.600	1.597	1.591	1.586
r_3	B3LYP/TZ2P	1.508	1.588	1.566		
r_3	BLYP/TZ2P	1.547	1.633	1.609		
r_3	B3LYP/TZ2P-ECP		1.571	1.566	1.561	1.555
r_3	BLYP/TZ2P-ECP		1.615	1.609	1.605	1.599
θ_1	B3LYP/DZP	116.6	113.6	119.2		
θ_1	BLYP/DZP	116.5	113.4	119.1		
θ_1	B3LYP/DZP-ECP		114.8	117.1	116.7	123.0
θ_1	BLYP/DZP-ECP		114.5	116.7	117.3	122.8
θ_1	B3LYP/TZ2P	116.7	113.7	119.2		
θ_1	BLYP/TZ2P	116.7	113.6	119.2		
θ_1	B3LYP/TZ2P-ECP		114.5	117.1	117.2	122.1
θ_1	BLYP/TZ2P-ECP		114.3	116.9	117.2	122.0

**Figure 2.** Trans–trans conformation for the group 14 congeners of dihydroxycarbene where X = C, Si, Ge, Sn, and Pb. The B3LYP/TZ2P optimized geometries are shown for X = C and the B3LYP/TZ2P-ECP optimized geometries are shown for X = Si–Pb. Table 1 gives the optimized geometries for all parameters with each method/basis used in this study. All congeners have C_{2v} symmetry and a 1A_1 electronic ground state.

decrease occurs for the Sn and Pb congeners. The angle in the Sn congener increases 3–4° from the Ge congener but then decreases by 1–2° for the Pb congener. This trend, explained by “hybridization defects,” is seen in other divalent group 14 molecules^{1,7,9,72} and is responsible for the distortion of the usually orthogonal hybrids seen in carbon. A similar trend occurs for the O–X–O angle (θ_2) as we descend group 14. The carbon congener has the largest angle of about 106° which is again nearly tetrahedral. This angle decreases by roughly 7–9° for the silicon congener and again by 2–4° for the germanium molecule. The decrease continues with a 2° decrease from Ge to Sn and then by only about 1° from Sn to Pb.

In the dioxirane congeners (Table 2 and Figure 3), similar trends are observed for the changes among DFT functionals

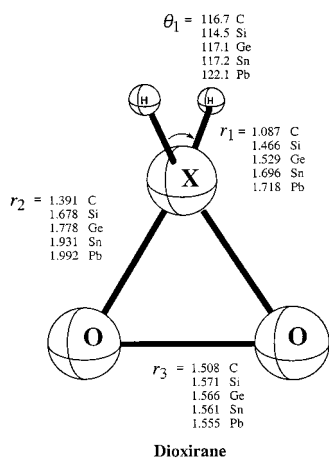


Figure 3. Group 14 congeners of dioxirane where X = C, Si, Ge, Sn, and Pb. The B3LYP/TZ2P geometries are shown for X = C, and the B3LYP/TZ2P-ECP geometries are shown for X = Si–Pb. Table 2 gives the optimized geometries for all parameters with each method/basis used in this study. All congeners have C_{2v} symmetry and a 1A_1 electronic ground state.

and basis set. For dioxirane (X = C) our results agree approximately with experiment. Microwave spectroscopic studies resulted in the following parameters: $r_1 = 1.0903$ Å, $r_2 = 1.388$ Å, $r_3 = 1.516$ Å, and $\theta_1 = 117.3^\circ$.¹⁶ Our B3LYP/TZ2P results yielded 1.087, 1.391, and 1.508 Å and 116.7° . The X–H (r_1) bond and the X–O (r_2) bond show the expected lengthening with the descent of group 14. After an initial increase from the C to the Si congener, the O–O (r_3) bond shows a steady decrease of about 0.006 Å for each congener from Si to Pb. The H–O–H angle (θ_1) shows a decrease of 3° from the carbon congener to the silicon congener but then increases by 3 – 6° for the germanium congener. The angle remains nearly the same for the X = Sn but increases by 5° for X = Pb. These differences are thought to be due to differences in the sizes (radial extensions) of the s and p orbitals in Pb over Sn.⁷

Comparison of bond lengths in like bonds among the four isomers provides some insight into the stability of the isomers. The X–OH bond is shorter in dihydroxycarbene than in formic acid. However, the X–OH bond tends to be shorter for the acid in X = Si–Pb. That is, only for X = C is the X–OH length shortest in the hydroperoxy congener. Clearly congeners of X = C are structurally different from the heavier group 14 congeners.

In our previous work,⁹ we found that the peroxy O–O single bond in hydroperoxycarbene congeners is quite typical for peroxy bonds, with a bond length of about 1.5 Å for every congener except X = C, in which case hydroperoxycarbene appeared to be a loose complex between the HCO and OH radicals and had an O–O bond length of about 1.8 Å. On the other hand, the dioxirane structure appears to be bound for all congeners. Thus for X = C the dioxirane O–O bond length is substantially shorter than that of hydroperoxycarbene but longer (by nearly 0.1 Å) for all other congeners. Likewise the X–O single bond in hydroperoxycarbene is significantly shorter than the X–O distances in dioxirane but nearly equivalent for X = Si and longer for X = Ge, Sn, and Pb. On the basis of these simple geometric observations, we might expect to see substantial changes in the relative differences in energetics between dihydroxycarbene and formic acid in moving from X = C to X = Si and between the dioxirane and hydroperoxycarbene structures in descending from X = Si to X = Ge.

3.2. Bonding. 3.2.1. NBO Analysis. As in our previous work, we employ natural bond order (NBO) analysis to obtain bonding

Table 3. Natural Atomic Charges (NAC) and Bond Orders (NPA) from the B3LYP/DZP and B3LYP/DZP-ECP Natural Bond Order (NBO) Analysis for the Dioxirane and Dihydroxycarbene Congeners

	NAC			NPA		
	X	O	H	X–O	O–H or O–O ^a	X–H
Dihydroxycarbenes						
C	0.43	–0.73	0.52	0.78	0.47	
Si	1.23	–1.13	0.51	0.38	0.48	
Si/ECP	1.21	–1.12	0.51	0.39	0.48	
Ge	1.20	–1.10	0.50	0.40	0.50	
Ge/ECP	1.25	–1.13	0.50	0.37	0.49	
Sn/ECP	1.35	–1.17	0.50	0.33	0.50	
Pb/ECP	1.33	–1.15	0.48	0.32	0.51	
Dioxiranes						
C	0.27	–0.30	0.16	0.70	1.00	0.80
Si	1.82	–0.56	–0.34	0.42	1.00	0.66
Si/ECP	1.60	–0.57	–0.23	0.41	1.00	0.76
Ge	1.42	–0.54	–0.16	0.45	1.00	0.82
Ge/ECP	1.57	–0.57	–0.22	0.42	1.00	0.77
Sn/ECP	1.88	–0.62	–0.32	0.37	1.00	0.67
Pb/ECP	1.54	–0.56	–0.21	0.42	1.00	0.76
$^3\Sigma_g^-, ^1\Delta_g O_2$		0.00			1.99	

^a O–O for dioxiranes.

information. Table 3 presents our NBO results for the dioxirane and dihydroxycarbene congeners. The charge on the group 14 atom in the dihydroxycarbene congeners is positive and ranges from 1.20 for Ge to 1.35 for Sn in the Si to Pb series. The carbon atom in contrast has only a 0.43 charge. The oxygen atom in dihydroxycarbene has a charge of -0.73 and is between -1.10 and -1.17 for Si–Pb. Clearly, the X–O bonds are highly polar. The trend in charges for dioxirane is similar for the group 14 elements but quite different for the oxygen: the charge on the oxygen remains -0.54 to -0.62 for the Si–Pb congeners. For the carbon congener the charge is only -0.30 on the oxygen and 0.27 on the carbon, indicating distinctly different bonding in the carbon congener than in the other dioxiranes.

3.2.2. Bond Strengths. In addition to the charge differences, we also note that the X–O bond order for the carbon congener of dioxirane is almost double (0.70) that of the other congeners (0.37 for Sn to 0.45 for Ge.) In all instances, however, the O–O bond order is 1.0 which is half that of free O_2 . Thus, all dioxirane congeners appear to be true molecules and not complexes between XH_2 and O_2 .

We estimated the dioxirane congener dissociation energies (obtained simply as the difference in absolute energies between dioxirane and the sum of the absolute energies of O_2 and the carbene fragment and reported without zero point correction). For the carbon case, both the carbene and the oxygen energy were determined in the triplet ground states. For Si–Pb, the carbenes as well as the oxygen energies were determined in the singlet state (1A_1 and $^1\Delta_g$, respectively). The singlet ground state of dioxirane suggested the choices of state for the metal carbene and oxygen dimer, as well as previous work that indicates the triplet state is lower than the singlet state of methylene but more than 23 kcal/mol higher for other group 14 carbenes.^{73–75}

The dissociation energies with BLYP/DZP and BLYP/DZP-ECP expressed in kcal/mol for the congeners of dioxirane from X = C to X = Pb are as follows: 90.4, 102.9, 77.4, 63.6, and 34.0.

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Table 4. Relative Energies in kcal/mol of Group 14 Isomers of XH_2O_2 , Formic Acid ($\text{H}(\text{X}=\text{O})\text{OH}$), Dioxirane (XH_2OO), and Hydroperoxide ($\text{H}\ddot{\text{X}}\text{OOH}$), Relative to the Dihydroxycarbene Congeners ($\ddot{\text{X}}(\text{OH})_2$) for the B3LYP, BLYP, CCSD, and CCSD(T) Methods Using the DZP, DZP-ECP, TZ2P, and TZ2P-ECP Basis Sets

	$\ddot{\text{X}}(\text{OH})_2$	$\text{HX}(=\text{O})\text{OH}$	XH_2OO	$\text{H}\ddot{\text{X}}\text{OOH}$
X = C				
B3LYP/DZP	0.0	-43.3	47.0	70.0
BLYP/DZP	0.0	-44.0	43.1	55.4
B3LYP/TZ2P	0.0	-43.2	51.4	67.8
BLYP/TZ2P	0.0	-43.8	47.1	52.6
CCSD/TZ2P//BLYP/TZ2P	0.0	-41.1	54.1	76.5
CCSD(T)/TZ2P//BLYP/TZ2P	0.0	-41.8	51.3	63.6
X = Si				
B3LYP/DZP	0.0	7.5	88.6	109.5
B3LYP/DZP-ECP	0.0	12.4	90.7	100.7
BLYP/DZP	0.0	5.9	83.3	102.4
BLYP/DZP-ECP	0.0	9.6	85.0	94.3
B3LYP/TZ2P	0.0	7.3	92.1	114.4
B3LYP/TZ2P-ECP	0.0	11.4	92.4	108.3
BLYP/TZ2P	0.0	6.0	87.2	107.0
BLYP/TZ2P-ECP	0.0	9.2	87.0	101.2
CCSD/TZ2P//BLYP/TZ2P	0.0	8.1	92.7	120.5
CCSD/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	9.4	91.7	115.6
CCSD(T)/TZ2P//BLYP/TZ2P	0.0	7.1	89.3	117.5
CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	7.9	88.0	112.6
X = Ge				
B3LYP/DZP	0.0	38.3	109.6	96.5
B3LYP/DZP-ECP	0.0	34.6	106.9	94.7
BLYP/DZP	0.0	36.1	105.1	91.4
BLYP/DZP-ECP	0.0	30.8	100.8	89.7
B3LYP/TZ2P	0.0	40.6	113.9	100.7
B3LYP/TZ2P-ECP	0.0	34.8	109.7	102.3
BLYP/TZ2P	0.0	38.4	109.4	95.5
BLYP/TZ2P-ECP	0.0	31.6	104.1	97.1
CCSD/TZ2P//BLYP/TZ2P	0.0	38.5	113.1	105.5
CCSD/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	32.4	108.6	107.9
CCSD(T)/TZ2P//BLYP/TZ2P	0.0	36.0	109.2	103.8
CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	30.0	104.5	105.8
X = Sn				
B3LYP/DZP-ECP	0.0	55.0	122.2	95.3
BLYP/DZP-ECP	0.0	49.1	114.8	90.7
B3LYP/TZ2P-ECP	0.0	55.3	125.9	103.0
BLYP/TZ2P-ECP	0.0	50.0	119.0	98.4
CCSD/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	53.8	125.8	108.4
CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	50.4	121.4	106.7
X = Pb				
B3LYP/DZP-ECP	0.0	76.8	144.8	89.6
BLYP/DZP-ECP	0.0	69.7	136.6	85.7
B3LYP/TZ2P-ECP	0.0	77.6	149.4	97.1
BLYP/TZ2P-ECP	0.0	71.1	141.6	93.2
CCSD/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	77.5	150.5	101.8
CCSD(T)/TZ2P-ECP//BLYP/TZ2P-ECP	0.0	73.6	145.5	100.5

Although the dioxirane congeners appear to be bound molecules (the O—O bond order is 1.0 for each congener, and the X—O distances are similar to those in $\text{H}\ddot{\text{X}}\text{OOH}$), it is clear they become increasingly less stable as one descends group 14. In contrast, $\text{H}\ddot{\text{X}}\text{OOH}$ congeners become more stable.⁹ Indeed, as we shall see in the next section, relative to its dihydroxide isomer, siladioxirane is about 90 kcal/mol less stable. However for lead, this difference is now 55 kcal/mol greater. This is not surprising when we note that the lead dioxirane species is over 65 kcal/mol less bound than siladioxirane.

3.3. Relative Energies. Previous work using G-2 theory by Darling and Schlegel determined the following energies relative to cis—trans dihydroxysilylene: 7.0, 89.6, and 117.3 kcal/mol for silanoic acid, siladioxirane, and hydroperoxysilylene, respectively.³⁸ Our energies relative to the trans—trans structure using CCSD(T)/TZ2P//BLYP/TZ2P were 8.1, 92.7, and 120.5 kcal/mol for the same isomers and 7.9, 88.0, and 112.6 kcal/mol using an ECP on Si. Our results agree well with G-2 theory, especially when lowering our energies by about 2 kcal/mol to

account for the difference between the cis—trans and trans—trans conformations of dihydroxycarbene. This suggests that the present results are valid, even with the ECP approximation.

Table 4 shows our results for the energies of the four XH_2O_2 isomers relative to the dihydroxycarbene congeners. In general, the relative energies among the isomers of the formic acid and the dihydroxycarbene congeners do not vary by more than 10 kcal/mol for all methods and basis sets within a given metal atom and method. However, for the dioxirane and the hydroperoxycarbene isomers variations of method and basis do produce larger variations in relative energies. Despite these variations, all relative energetic trends among isomers of a particular metal atom do remain qualitatively the same. Certainly the use of an ECP can reduce the reliability of our relative energetics and give the variation seen among the results for X = Si and X = Ge. However, our CCSD(T) results do not vary by more than 6 kcal/mol for X = Si and X = Ge, whether an ECP is used. Thus, as already suggested, the ECP results seem reliable and are probably within a 10 kcal/mol error bar.

Consistent with the geometry changes noted in section 3.1, the formic acid isomer lies lower in energy than dihydroxycarbene by 41.8 kcal/mol for $X = C$. This CCSD(T)/TZ2P//BLYP/TZ2P relative energy difference compares to a previous theoretical determination of 41.7 kcal/mol for PMP4/6-311++G**//UMP2/6-311G**.¹⁴ For the $X = Si$ the dihydroxycarbene congener is lower than the formic acid congener by about 8 kcal/mol. The difference increases to about 74 kcal/mol for $X = Pb$. The other divalent isomer, hydroperoxycarbene, remains a consistent 100–113 kcal/mol higher than the dihydroxycarbene for all but the $X = C$ congener where the difference is only 64 kcal/mol. An O–H substituent of dihydroxycarbene would seem to yield more stability than the O–O–H group with its weak O–O bond in the hydroperoxycarbene.

The dioxirane congeners become increasingly more unstable for the heavier members of group 14 with the lead congener lying 146 kcal/mol higher in energy than its dihydroxy isomer and, consistent with section 3.1, become less stable than the hydroperoxycarbene congeners for $X = Ge$ – Pb . The instability of heavier dioxirane congeners is also consistent with the decrease in dissociation energies noted in section 3.2.2. In general, our results show that divalency is more favored or at least less disfavored in moving down group 14, although the stability of the acid congeners shows that not all divalent isomers are more stable than their corresponding tetravalent isomers. The O–H substituent increasingly stabilizes the divalent species

with respect to tetravalency for the heavier congeners. This preference for divalency is in agreement with previous work of Kapp et al., who showed that the simpler divalent $H\ddot{X}OH$ species are favored over tetravalent $H_2X = O$ isomers in all cases except $X = C$.¹

4. Conclusions

The group 14 congeners for molecules of the form XH_2O_2 provide insight into the nature and stability of the bonding in group 14 elements. In this study, our previous investigation,⁹ and the work of Kapp et al.¹ the stability of particular isomers appears to be related to the nature of the ligands attached to the central metal atom. The tetravalent formic acid is most stable for carbon. In contrast, the divalent dihydroxy congeners are most stable for all other group 14 atoms. However, the tetravalent acid is still more stable than the divalent hydroperoxy isomers in all instances, though the latter does increase in stability relative to the acid. Our results show that divalency is either preferred or at least more favored as one descends group 14. In addition, many of the isomers in this study could be interesting molecules for spectroscopic investigation. Certainly new investigations into the nature of divalent and tetravalent group 14 molecules are warranted.

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