Ab Initio Molecular Orbital Study of the Reaction of GeH$_2$ with H$_2$O and Decomposition Reactions of H$_3$GeOH

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Received: October 9, 2000; In Final Form: December 7, 2000

The formation of H$_3$GeOH from GeH$_2$ and H$_2$O and its decomposition paths have been studied using the G2 molecular orbital method. It is predicted that GeH$_2$ reacts with H$_2$O exothermically (by 10.0 kcal mol^{-1}) without a barrier to form a nonplanar complex, H$_2$GeOH$_2$, which isomerizes via a 1,2-H shift to H$_3$GeOH with a barrier of 28.3 kcal mol^{-1}. The backward isomerization requires an activation energy of 61.1 kcal mol^{-1}. In addition, direct decompositions of H$_3$GeOH yielding H$_3$GeO + H, H$_3$Ge + OH, and H$_2$GeOH + H are shown to have large endothermicities of 113.7, 102.4, and 84.9 kcal mol^{-1}, and those producing H$_2$GeO + H$_2$ and HGeOH + H$_2$ to have activation energies of 82.1 and 57.6 kcal mol^{-1}, respectively. Hence, H$_3$GeOH is stable to the above decomposition processes unless its temperature is moderately high or above.

Introduction

The oxidation of silicon species in an anaerobic environment has been suggested by Zachariah et al.,[1] on the basis of their works,[2−4] to occur in the presence of water vapor. They have also proposed that the singlet silylene, SiH$_2$, must be directly involved in the oxidation because it is known to be the primary product of silane pyrolysis. Theoretically, the reaction of SiH$_2$ with H$_2$O has been shown[1,5] to form, without barrier, a nonplanar intermediate complex, H$_2$SiOH$_2$, which then isomerizes to silanol, H$_3$SiOH, with an activation barrier of 2.5 kcal mol^{-1} at the MP4/6-311G(2df,p)//MP2/6-31G* + ZPE (HF/6-31G* frequencies scaled by 0.89) level[1] (8.7 kcal mole^{-1} at HF/6-31G*[5]).

Silanol itself is a molecule of considerable interest. It is the simplest species having a SiO single bond. In addition, it is the simplest prototype for silicic acid, Si(OH)$_4$, and the starting molecule for other interesting processes. Thus, the thermal decomposition reactions (corresponding to reactions 2−6 shown below for H$_3$GeOH) of silanol have been studied by ab initio calculations[1,6] in order to gain some insight of the SiO bond reactivity and the nature of the SiO bond.

As for the germanium counterparts of the above species, less work has been reported in the literature. Germylene, GeH$_2$, has been studied many times.[7] However, no report on its direct reaction with water is noted. Whitnall and Andrews[8] have studied the IR spectra of products produced from UV photolytic reactions of a germane and ozone mixture in low-temperature argon matrix and identified seven new molecular product species including the H$_2$GeOH$_2$ complex, germanol, H$_3$GeOH, hydroxy-germylene, HGeOH, and germanone, H$_2$GeO. Recently, H$_2$GeOH$_2$ has been shown[9] by DFT and ab initio calculations to have a nonplanar equilibrium geometry with a GeO distance of 2.214−2.286 Å, depending on the levels of theory employed, though Whitnall and Andrews[8] have suggested a planar one to be a possible structure.

It was thus thought desirable to study theoretically the reaction of GeH$_2$ with H$_2$O

$$GeH_2 + H_2O \xrightarrow{(1a)} H_2GeOH_2 \xrightarrow{(1b)} H_3GeOH \qquad (1)$$

and the decomposition reactions of H$_3$GeOH formed

$$H_3GeOH \rightarrow H_2GeO + H_2 \qquad (2)$$

$$\rightarrow HGeOH + H_2 \qquad (3)$$

$$\rightarrow H_3GeO + H \qquad (4)$$

$$\rightarrow H_2GeOH + H \qquad (5)$$

$$\rightarrow H_3Ge + OH \qquad (6)$$

Calculations

The structures of the various species studied were optimized by the energy gradient method at the restricted (for closed shells) and unrestricted (for open shells) HF/6-31G* and MP2(FU)/6-31G* levels of theory (FU denotes "full", meaning inclusion of both inner shell and valence electrons), using the Gaussian 98 programs[10] implemented on our DEC 500 and 600 AU, and COMPAQ XP1000 workstations.

The energies of the above optimized stationary point structures were computed at the Gaussian-2 (G2) theory,[11] which is the improved Gaussian-1 (G1) theory.[12,13] The conventional G2 method uses a series of frozen-core (FC) QCISDT, MP4SDTQ, and MP2 single-point energy calculations on the MP2(FU)/6-31G* structures with various basis sets to approximate a full QCISDT(FC)/6-311+G(3df,2p)//MP2(FU)/6-31G* calculation, incorporating a so-called "higher order correction" based on the number of paired and unpaired electrons and scaled HF/6-31G* zero-point vibrational energies. However, in the present work, MP2(FU)/6-31G* zero-point vibrational energies scaled by a factor of 0.9427[14] were used instead. Furthermore, the 3d orbitals of the Ge atom of a species were also not kept frozen in the FC

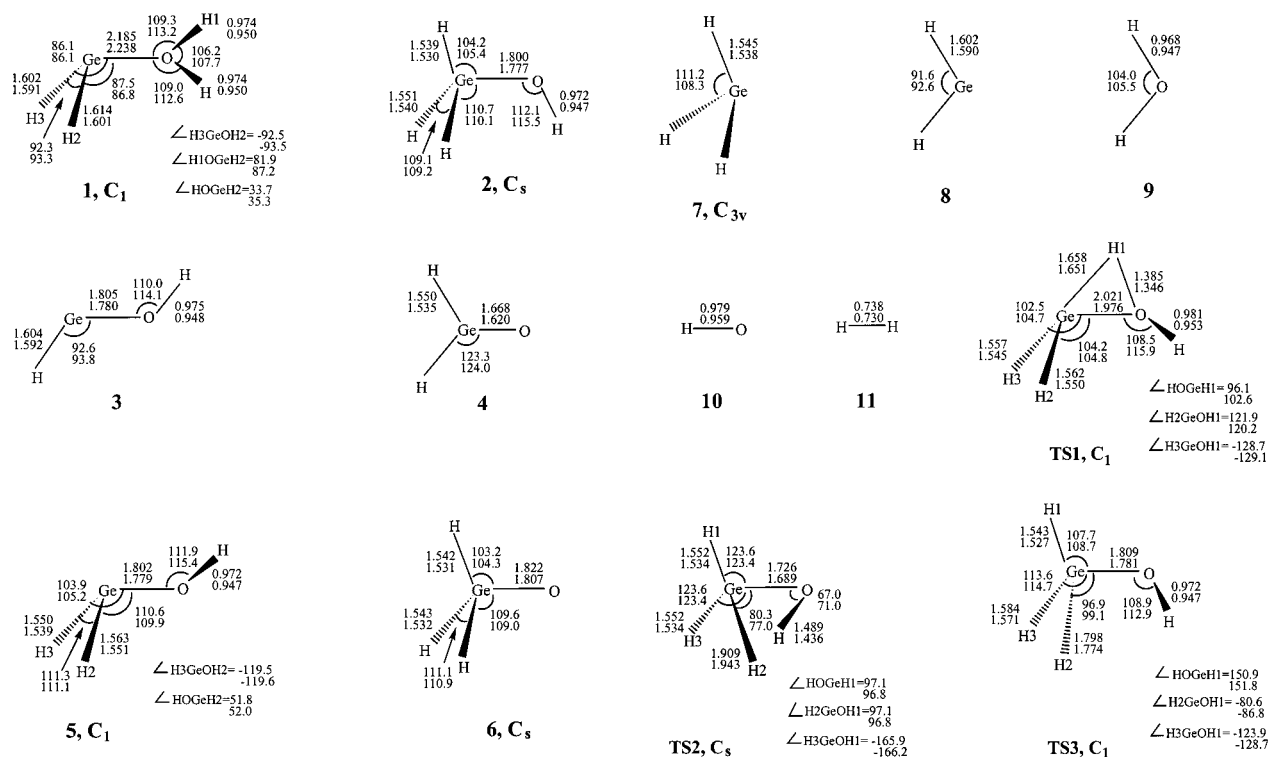* Fax: +852-2603-5057. E-mail: sukpingso@cuhk.edu.hk.

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Figure 1. Optimized structures of species studied. Bond lengths are in angstroms and angles in degrees. MP2(FU)/6-31G* values are shown above the HF/6-31G* values.

single-point energy calculations because correlating these orbitals has been found to be important in the calculations of $Ge_3H_3^+$ isomers.[15]

The various basis sets for G2 calculations of compounds containing third-row elements have been developed by Curtiss et al.[16-18] and shown to give energy results with an average absolute deviation of 1.37 kcal mol⁻¹ from experiment for 40 test reactions.

Vibrational frequencies were determined by the analytical evaluation of the second derivatives of energy to verify the nature of the stationary point structures, to provide zero-point vibrational energy corrections, and to predict vibrational frequencies of the unknown stable species for the sake of their future identification by infrared spectroscopy.

The connection between each transition state structure and the reactants and products was established at the MP2(FU)/6-31G* level of theory, by intrinsic reaction coordinate (IRC) calculations based on the reaction path following algorithm of Gonzalez and Schlegel[19,20] as coded in Gaussian 98, or by optimization starting from a transition state structure with one or two of its geometrical parameters distorted.

Results and Discussion

The various stationary point structures studied are depicted in Figure 1 together with their optimized geometrical parameters. The calculated structures have been shown to be either equilibrium structures (**1−11**) or transition state structures (**TS1−TS3**) by both their HF/6-31G* and MP2(FU)/6-31G* vibrational frequencies. Structures **TS1**, **TS2**, and **TS3** are the transition state structures for the reactions 1b, 2, and 3, respectively. Table 1 lists the scaled MP2(FU)/6-31G* harmonic vibrational frequencies of the stable Ge species studied together with experimental values available.[8] Because the reported observed frequencies are for fundamental bands of the species in argon matrix, the agreement between the predicted and the observed frequencies is considered to be reasonable.

TABLE 1: MP2(FU)/6-31G* Harmonic Vibrational Frequencies^a of the Stable Ge Species Studied

species	frequencies (cm⁻¹)
H₂GeOH₂	135, 271, 473, 508, 650, 734, 902(897.8)^b,1606(1586.1), 1729(1777.2), 1781(1813.6), 3511(3597.4), 3632(3686.0)
H₃GeOH	184, 586, 605, 685(688.6), 832(871.7), 834(867.6), 856(877.2), 919(924), 1977, 1980, 2034, 3585
HGeOH	639(566.0), 671(661.0), 724(708.7), 923(885.2), 1775(1741.1), 3548(3652.0)
H₂GeO	546, 553, 837(803.8), 900(961.9), 1969(2079.6), 1974(2076.6)
H₂GeOH	255(OH wag), 589(GeH₂ twist), 663(GeH₂ wag), 685(GeH₂ sym bend + GeO str), 801(GeH₂ scis), 905(OH bend), 1895(GeH str), 1973(GeH str), 3575(OH str)
H₃GeO	396(a″:GeH₂ rock), 521(a′:GeH₂ wag + GeH bend), 667(a′:GeO str + GeH bend), 812(a′:GeH₂ wag − GeH bend), 818(a″:GeH₂ asym bend + GeH wag), 851(a′:GeH2 sym bend),2002(a′:GeH₂ sym str + GeH str), 2011(a″:GeH₂ asym str),2021 (a′:GeH₂ sym str − GeH str)
H₃Ge	665(a₁:GeH₃ sym def), 826(e:GeH₃ asym def), 1966(a₁:GeH₃ sym str), 2006(e:GeH₃ asym str)
H₂Ge	913(a₁:GeH₂ bend), 1788(a₁:GeH₂ sym str), 1805(b₂:GeH₂ asym str)

^{a} Frequencies have been uniformly scaled by a factor of 0.9427. Descriptions of the vibrational modes of H₂GeOH₂, H₃GeOH, HGeOH and H₂GeO are given in refs 8 and 9. ^{b} Observed values from ref 8 are in parentheses.

The ⟨S²⟩ values obtained from unrestricted HF/MP2 wave functions are 0.755/0.755 for OH, 0.755/0.754 for H₃Ge, 0.758/0.758 for H₃GeO, and 0.754/0.754 for H₂GeOH, respectively. These are almost identical to the value of 0.75 of a pure doublet state. Hence, for these species, the unpredictable spin contamination effect due to unrestricted wave functions on molecular geometry[21] may be neglected.

It is significant to note from Figure 1 that the inclusion of electron correlation up to the MP2 level in geometry optimiza-

tion gives the expected small changes in the bond lengths and bond angles (~0.05 Å and ~5° or less) except the GeOH and HOGeH1 angles of **TS1**. These parameters undergo a change as large as about 7.4° and 6.5°, respectively (Figure 1).

As predicted by Nowek et al.,[9] the H_2GeOH_2 complex formed from GeH_2 and H_2O is found to have, like H_2SiOH_2, a nonplanar equilibrium structure of C_1 symmetry. It is interesting to note that the GeH_2 and H_2O subunits undergo only a very small change in geometry (not more than 0.012 Å and 2.2° at the MP2(FU)/6-31G* level) on complex formation (Figure 1). It is thus no wonder that the GeO bond of the complex (2.185 Å) has been computed to be much longer than the expected GeO double bond of H_2GeO (1.668 Å) and the GeO single bond of H_3GeOH (1.800 Å).

In the search for the equilibrium structure of H_3GeO, geometry optimization was first carried out under the constraint of C_{3v} symmetry. The $C3_v$ geometry of H_3GeO would be expected to undergo a Jahn−Teller distortion, in view of its anticipated[22] ground state electronic configuration ··· (e).[3] Accordingly, optimization was performed using complete active space SCF (CASSCF) wave functions with an active space comprising three electrons in four active orbitals. The latter were selected according to the procedure suggested by Pulay and Hamilton[23] based on the fractional occupations of the natural orbitals of the UHF wave functions (UNOs). The atomic charges on the H atoms obtained are −0.0059, 0.0079, and 0.0079, indicating the wave functions to be of C_s symmetry. Thus, H_3GeO was reoptimized with C_s symmetry contraint, yielding a structure in an $^2A'$ state which has an energy (−2149.826406 hartrees) lower than that (−2149.818537 hartrees) of the C_{3v} structure. The geometrical parameters of the $^2A'$ H_3GeO were found to distort only slightly from those of the C_{3v} structure except a much smaller unique HGeO bond angle. Similarly, H_3CO has also been computed[24−26] to have a $C_s$$^2A'$ ground electronic state with a small geometry distortion from C_{3v} symmetry. Thus, a small Jahn−Teller distortion is predicted here to be also present in the C_{3v} H_3GeO, as in the carbon analogue.[24−26] It should be mentioned that calculations in this work have also yielded similar results for H_3SiO, though only a theoretical C_{3v} geometry has been reported in the literature.[1,6] The CASSCF(3,3)/6-31G* C_s structure of H_3GeO was found to have a geometry very similar to the UMP2(FU)/6-31G* one, with a difference of not over 0.015 Å and 1.5 degrees for a bond length and a bond angle, respectively. This is in line with the theoretical results that the former structure has a coefficient of about 0.99 for the reference configuration, and the latter structure a $\langle S^2 \rangle$ value (0.758) very close to 0.75. Thus, the energy for $^2A'$ H_3GeO was calculated, for comparison purpose, at the G2 level based on the unrestricted single-determinant MP2 geometry.

The structure of H_2GeOH, as shown in Figure 1, is nonplanar with C_1 symmetry as in the cases of H_2COH^{25} and H_2SiOH.[6] Its GeO bond is predicted at the MP2(FU)/6-31G* level to be 1.802 Å long. However, its cation (or protonated H_2GeO), H_2GeOH^+, has been shown,[22] at the MP2(FU)/3-21G$^{(*)}$ level of theory, to be planar with a much shorter GeO bond of 1.719 Å, which is close to the GeO double bond length (1.620 Å) of H_2GeO. The non-C_s symmetry of H_2GeOH arises probably from the minimization of the interaction between the oxygen lone-paired electrons and the GeH bonds.

The transition state structure, **TS3**, for the 1,1-H_2 elimination reaction of H_3GeOH (Figure 1) shows that the two hydrogen atoms prefer to leave in an asymmetric manner. Same results have also been found for this process in H_3SiOH^6 and H_2GeO.[27]

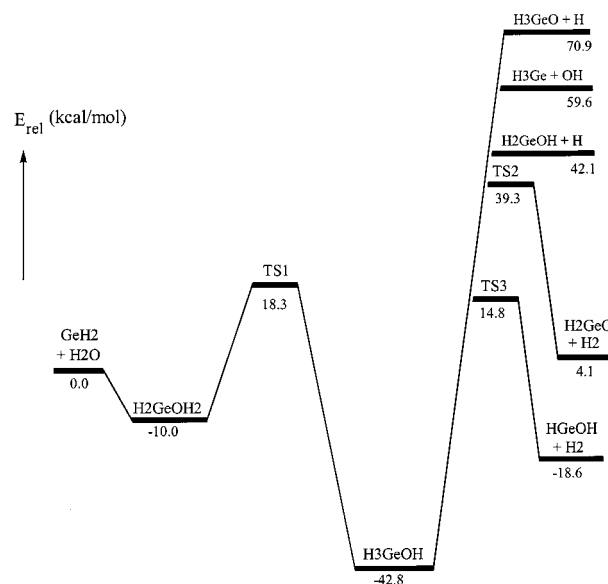**Figure 2.** Schematic G2 potential energy profiles for the GeH2 + H2O reaction and decomposition paths of H3GeOH.

TABLE 2: G2 Total Energies of Species Studied

species	energy (hartrees)
H_2GeOH_2	−2153.089131
H_3GeOH	−2153.141392
HGeOH	−2151.936643
H_2GeO	−2151.900503
H_2GeOH	−2152.505985
H_3GeO	−2152.460156
H_3Ge	−2077.334115
H_2Ge	−2076.740817
H_2O	−76.332313
OH	−75.644004
H_2	−1.166073
H	−0.500000
TS1	−2153.043943
TS2	−2153.010567
TS3	−2153.049562

In the study of reactions 1a and 1b, it has been found that the reaction of GeH_2 and H_2O to form the H_2GeOH_2 complex is barrierless, whereas the isomerization of H_2GeOH_2 to H_3-GeOH via a 1,2-H shift has an activation barrier. Thus, reaction 1b is the rate-determining step for the formation reaction of H_3GeOH from GeH_2 and H_2O. The G2 total energies of the species studied are listed in Table 2, from which H_2GeOH_2 is found to have a binding energy of 10.0 kcal mol^{-1} and to be less stable than H_3GeOH by 32.8 kcal mol^{-1}. Figure 2 displays the G2 potential energy profiles for the GeH_2 + H_2O reaction and the decomposition reactions of H_3GeOH. It is seen that both reactions 1a and 1b are exothermic by 10.0 and 32.8 kcal mol^{-1} with reference to the energies of their reactants, respectively. The barrier to the formation of H_3GeOH is not large, viz., 28.3 kcal mol^{-1} relative to the energy of H_2GeOH_2 (reaction 1b) or 18.3 kcal mol^{-1} relative to the energy sum of GeH_2 and H_2O (Figure 2). The corresponding values for the Si analogue were computed in this work at the same G2 level to be 21.0 and 9.6 kcal mol^{-1} (but only 2.5 kcal mol^{-1} at MP4/6-311G(2df,p)// MP2/6-31G* + ZPE(HF/6-31G*)[1] or 8.7 kcal mol^{-1} at HF/6-31G*[5]). Thus, H_2GeOH_2 and H_2SiOH_2 have similar binding energies (10.0 and 11.3 kcal mol^{-1}), but the former has a larger barrier to its 1,2-H shift than the latter. It is significant to note that the formation of H_3COH from $^1CH_2$ and H_2O is barrierless and thus there is no intermediate.[28] The endothermicity for reaction 1a to proceed backward is only 10.0 kcal mol^{-1}, but

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the activation barrier for the isomerization of H$_3$GeOH back to H$_2$GeOH$_2$ is very high, viz., 61.1 kcal mol^{-1}. Hence, the decomposition of H$_3$GeOH to GeH$_2$ and H$_2$O via H$_2$GeOH$_2$ is not favored both thermodynamically and in terms of activation energy. The low forward and high backward barriers of reaction 1b obtained above are in line with the observation of H$_2$GeOH$_2$ and H$_3$GeOH produced by the photolysis of a mixture of GeH$_4$ and O$_3$ at 380−633 nm and support the suggested mechanism that H$_3$GeOH was formed from the mixture via the H$_2$GeOH$_2$ intermediate.[8]

As for the direct decomposition channels of H$_3$GeOH studied in this work, reactions 4−6 are homolytic cleavages of a single bond (H− or OH elimination) and are expected to be endothermic reactions without activation barriers. Indeed, it has been found here at the MP2(FU)/6-31G* level that the energy of H$_3$-GeOH is still rising when the bond to be cleavaged in reactions 4−6 is extended up to about 3−4 Å. Figure 2 reveals that the endothermicities of reactions 4, 5, and 6 are 113.7, 84.9, and 102.4 kcal mol^{-1} at the G2 level, respectively. Hence, these H- and OH-elimination reactions are feasible only at high temperatures.

Reactions 2 and 3 studied are the 1,2-H$_2$ and 1,1-H$_2$ eliminations and are predicted in this work to have activation barriers of intermediate values, viz., 82.1 and 57.6 kcal mol^{-1} at the G2 level, respectively. These reactions are thus expected to occur at moderately high temperature, the 1,1-H$_2$ elimination being energetically more feasible because of its lower barrier. However, the respective barriers for the product species of these reactions to recombine to form H$_3$GeOH are much lower, viz., 35.2 and 33.4 kcal mol^{-1}. Consequently, H$_3$GeOH, even if decomposed in reactions 2 and 3, will be readily formed again by the reverse reactions.

The above energetic ordering in terms of endothermicity or activation energy for the unimolecular decomposition reactions 2, 3, 4, and 5 of H$_3$GeOH is the same as that of H$_3$COH.[28] However, reaction 2 of H$_3$SiOH was found to have an activation energy larger (by 1.29 kcal mol^{-1} at MP4/6-311G(2df,p)//MP2/6-31G* + ZPE(HF/6-31G*)) than that of reaction 3, being the reverse of the ordering for H$_3$COH[28] and H$_3$GeOH.

As a conclusion, the above results have shown that H$_3$GeOH is rather stable at ordinary temperatures toward the various decomposition processes considered.

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