Ab Initio Molecular Orbital Study of TiH$_2$O and TiH$_3$OH

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Ab initio electronic structure calculations are reported for TiH$_2$O and TiH$_3$OH, the simplest prototypical molecules containing Ti═O and Ti−O bonds, respectively, with particular focus on the unimolecular decomposition mechanisms of TiH$_3$OH and the isomerization of TiH$_2$O. The equilibrium structures in the ground and lowest excited states and the potential energy surfaces for various unimolecular decomposition reactions are investigated, with the effects of electron correlation included. At the highest levels of theory (multiconfigurational wave functions augmented by second-order perturbation theory), singlet TiH$_2$O is predicted to be the global minimum on its potential energy surface, and TiH$_3$OH is predicted to be stable to unimolecular decomposition.

I. Introduction

Titanium compounds are well-known as catalysts in a wide variety of organometallic reactions, including, for example, the hydrosilation[1] and silane polymerization[2] reactions. Ti compounds containing oxygen, such as Ti(OR)$_4$ (titanium alkoxides)[3] or titanosilicate,[4] have attracted considerable attention as important precursors of glasses and ceramics or as an adsorption model in zeolite frameworks. Furthermore, Ti−Si mixed oxides[5] or titanosilsesquioxanes[6] are also of interest, because of their potential as new catalysts. In addition, thermal decompositions of these compounds are important as initial steps in the chemical vapor deposition of Ti and TiO.

Previously,[7] we have investigated the molecular structure of TiH$_3$X, including X = OH, in some detail. In view of the relation to chemical vapor deposition processes, in the present investigation, we have undertaken ab initio electronic structure calculations of the molecular and electronic structure and stability with respect to unimolecular reactions, of the simplest prototypical titanium−oxygen singly bonded compound, TiH$_3$-OH. The main focus in this work is on the unimolecular kinetic stability of TiH$_3$OH. Furthermore, the titanium analogue of formaldehyde, TiH$_2$O, has also been investigated because it is the simplest titanium−oxygen doubly bonded molecule and one of the fragment molecules produced in the decomposition of TiH$_3$OH. There have been many experimental studies of titanium complexes containing titanium−oxygen multiple bonds.[8] However, there have been no experimental or theoretical studies on isolated titanium−oxygen doubly bonded species such as TiR$_2$O or TiRR′O.

This paper is organized as follows: Following a summary of the computational methods that were employed (section II), the structure of TiH$_2$O in its ground and excited states are compared with those of the silicon and carbon analogues (section IIIA). The 1,2-hydrogen transfer reaction leading from TiH$_2$O to the divalent titanium isomer, HTiOH, is also discussed in section IIIA. The structure and the potential energy surfaces for several decomposition reactions of TiH$_3$OH (shown in

SCHEME 1
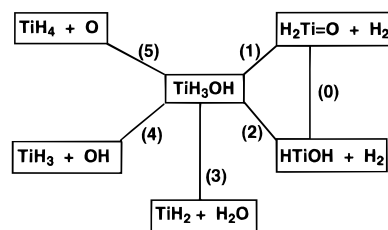
Scheme 1) are discussed in Section IIIB. A summary and conclusions are presented in section IV.

II. Computational Methods

Geometries were optimized at the Hartree−Fock (HF), the second-order perturbation (MP2),[9] and complete active space self-consistent field (CASSCF)[10] levels of theory. For TiH$_3$-OH, a full valence space corresponds to 14 electrons and 14 orbitals, denoted CASSCF (14/14). The notation (*m*/*n*) means *m* electrons and *n* orbitals are included in the active space. However, even for the smaller CASSCF(12/13) active space, constructed by deleting the oxygen 2s orbital and accompanying 2 electrons from the full valence (14/14) active space, the calculations are beyond our computational capabilities. Therefore, we have used the (12/12) active space, obtained by deleting the Ti virtual 3d$_{x^2-y^2}$ orbital from the (12/13) space (The Ti−O bond is on the *Z* axis). Based on preliminary CASSCF calculations, this orbital is found not to be essential for a description of the present system. Table 1 summarizes the active spaces used for the CASSCF calculations for each reaction of interest. For TiH$_2$O, a (10/11) active space was constructed by removing the oxygen 2s orbital and its 2 electrons from the full valence (12/12) active space.

The basis set used in this work is the triple-ζ plus polarization (TZVP) basis set developed by Wachters[11] and Goddard.[12] Furthermore, the 6-311G(d,p) basis set[13] was used for the MP2 optimization of H$_2$X═O and H$_3$X−OH (X = C and Si), for

TABLE 1: Active Spaces Used for the CASSCF Geometry Optimizations

reaction[a]	size of the active space for individual molecules[b]
0	$H_2Ti=O \leftrightarrow HTiOH$
	(10/11)　　(10/11)
1	$TiH_3OH \leftrightarrow H_2Ti=O + H_2$
	(12/12)　　(10/10)　　(2/2)
2	$TiH_3OH \leftrightarrow HTiOH + H_2$
	(12/12)　　(10/10)　　(2/2)
3	$TiH_3OH \leftrightarrow TiH_2 + H_2O$
	(12/12)　　(6/7)　　(6/5)
4	$TiH_3OH \leftrightarrow TiH_3 + OH\ (^2\Pi)$
	(12/12)　　(7/8)　　(5/4)
5	$TiH_3OH \leftrightarrow TiH_4 + O(^1D)$
	(12/12)　　(8/9)　　(4/3)

[a] See Scheme 1. [b] See the text for notation.

TABLE 2: TZVP Optimized[a] Geometries (angstroms and degrees) of Titanone (H_2TiO) at Several Computational Levels in the Ground Singlet and Lowest Excited Triplet States

level	r(TiO)	r(TiH)	∠HTiO	∠HTiH	θ^b
$^1A'$					
RHF	1.573	1.751	116.5	127.0	0.0
CASSCF(10/10)	1.614	1.795	111.4	124.2	38.9
CASSCF(10/11)	1.622	1.796	112.3	126.2	38.1
MP2	1.631	1.762	106.5	124.6	52.2
$^3A'$					
planar					
CASSCF(10/10)	1.653	2.042	152.8	54.4	0.0
CASSCF(10/11)	1.653	2.028	153.8	52.5	0.0
bent					
CASSCF(10/10)	1.656	2.057	159.4	23.4	17.1
CASSCF(10/11)	1.657	2.053	162.9	23.3	12.6
$^3A''$					
planar					
CASSCF(10/10)	1.653	2.042	153.6	52.9	0.0
bent					
CASSCF(10/10)	1.652	1.993	134.0	24.4	44.7
CASSCF(10/11)	1.653	1.994	132.6	24.9	46.1

[a] The nature of the stationary points is shown in Table 5. [b] Angle between the HTiH plane and TiO axis.

comparison with the Ti analogue. All stationary points were characterized as minima or transition states by calculating and diagonalizing the Hessian (matrix of energy second derivatives). For CASSCF wave functions, the Hessian was obtained numerically from finite differences of analytic gradients. Analytic Hessians for other Hartree–Fock and MP2 calculations were determined using the electronic structure codes GAMESS[14] and GAUSSIAN92, respectively.[15] Final energetic comparisons are made with fourth order perturbation theory (MP4),[16] multireference second-order perturbation theory (CASPT2),[17] coupled cluster with single, double and perturbative triple excitations (CCSD(T)),[18] and the analogous quadratic configuration interaction method (QCISD(T))[19] using the same basis sets. CASPT2 calculations were performed using the MOLCAS program.[20]

III. Results and Discussion

A. TiH$_2$O. *Titanone and the Divalent Isomer.* The optimized geometries of H_2TiO (titanone), within C_s symmetry constraints at various levels of theory, are presented in Table 2. The number of imaginary frequencies for each structure (indicating the nature of the stationary point) is given with the

TABLE 3: Comparison of the MP2/TZVP $^1A'$ Bond Lengths, Net Atomic Charges, and Dipole Moments for $H_2X=O$ (X = C, Si, and Ti)[a]

	bond lengths (Å)		Δ	net atomic charges			dipole moment
X	r(X=O)	r(X–O)[b]	(%)[c]	X	O	H	(D)
C	1.211	1.418	14.6	0.102	−0.239	0.068	2.171
Si	1.535	1.659	7.5	0.825	−0.507	−0.159	3.335
Ti	1.631	1.766	7.6	0.713	−0.264	−0.224	3.636

[a] 6-311G(d,p) for H_2CO and H_2SiO. [b] The X–O single bond length in H3X–OH (X = C, Si, and Ti). [c] $(r(X-O) - r(X=O))100/r(x-O)$.

TABLE 4: TZVP Optimized Geometries (angstroms) of HTiOH[a] at Several Computational Levels in the Lowest Excited Singlet and Ground Triplet States

level	r(TiO)	r(TiH)	r(OH)
$^1A'\ (^1\Sigma^+)$			
RHF	1.882	1.900	0.954
CASSCF(10/10)	1.893	1.910	0.953
CASSCF(10/11)	1.891	1.895	0.956
MP2	1.880	1.877	0.951
$^3A'\ (^3\Delta)^b$			
CASSCF(10/10)	1.890	1.877	0.956
CASSCF(10/11)[c]	1.890	1.877	0.956
$^3A''\ (^3\Delta)^b$			
CASSCF(10/10)	1.890	1.877	0.956
CASSCF(10/11)[c])	1.890	1.877	0.956

[a] All geometries are linear. [b] The triplet A′ and A″ states in the C_s symmetric structures are degenerate (Δ) in the linear $C_{\infty v}$ structure. [c] State averaged optimizations.

TABLE 5: The CASSCF and CASPT2 Relative Energies (kcal/mol) and the Number of Imaginary Frequencies[a] of TiH$_2$O and HTiOH in Singlet and Triplet States

	CASSCF		CASPT2[b]
state	(10/10)	(10/11)	(10/11)
$H_2Ti=O$			
$^1A'$	0.0 (0)	0.0 (0)	0.0
$^3A'$ planar	51.8 (0)	54.6 (1)	
bent	44.6 (1)	46.6 (1)	
$^3A''$ planar	52.0 (0)		
bent	42.9 (1)	37.1 (?)[c]	42.5
HTiOH			
$^1A'\ (^1\Sigma^+)^d$	0.0 (0)	0.0 (0)	0.0
$^3A'\ (^3\Delta)^d$	−25.9 (0)	−24.5	−18.0
$^3A''\ (^3\Delta)^d$	−25.9 (0)	−24.5	−18.0

[a] The values are in parentheses. [b] Single point energies on the CASSCF(10/11) geometries. [c] The hessian for this structure was not determined, since it dissociates without barrier. [d] Nomenclature for linear ($C_{\infty v}$) structures.

energetic data in Table 5. The Ti–O bond is on the Z axis. In the CASSCF(10/10) wave function, one virtual $3d_{x^2-y^2}$ or $3d_{xy}$ orbital on titanium atom is removed from the largest (10/11) active space, to be consistent with the TiH$_3$OH active space discussed in section II.

In the singlet state, the calculations including electron correlation (CASSCF and MP2) predict a longer Ti–O bond length, compared with that predicted at the HF level. This is expected, since the correlated wave functions include TiO antibonding contributions. The calculated Ti–O bond length (1.631 Å) is close to the DFT[4d−f] and experimental[21] values. No significant difference is seen between the CASSCF(10/11) and (10/10) geometries, thus validating the use of the smaller active space. The most dramatic difference between the HF and correlated levels is seen in the bond flapping angle θ that measures the deviation of the molecule from planarity ($\theta = 0$). Titanone has a planar C_{2v} structure only at the HF level.

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Preliminary calculations reveal that the molecule is almost planar if a smaller CASSCF active space is used, in which the two 1s hydrogen orbitals (σ_{Ti-H}) are not included. The σ_{Ti-H} (a″) orbital with antibonding character between the two hydrogen atoms appears to play an important role in determining the planarity of the Ti atom. The single configuration MP2 level of theory predicts the singlet state to be even more bent than does CASSCF.

Table 3 compares the bond lengths, net atomic charges, and dipole moments of titanone with those of silanone (H₂SiO) and formaldehyde obtained at comparable calculational levels. Among the three species, only titanone has a nonplanar ground state structure. Generally, the properties of titanone are similar to those of silanone: a relatively weak double bond, as measured by Δ (Table 3), the percent decrease in the XO double bond length relative to the single bond length; a highly polar X⁺−O⁻ double bond; and similar dipole moments, about 1 D larger than the dipole moment in formaldehyde.

In the excited ³A′ and ³A″ states (Table 2), titanone has significantly longer Ti−H bond lengths and smaller HTiH bond angles compared with those in the ground ¹A′ state. This may be understood by noting that the main electronic configurations of the triplet states are one electron excitations from the σ_{Ti-H} orbital with H−H antibonding character into the δ type 3d orbitals—$d_{x^2-y^2}$ (³A′) or d_{xy} (³A′)—on Ti atom. Such excitations weaken the Ti−H bonding and strengthen the H−H interaction. Indeed, the H−H distance is very short in these structures, which therefore resemble complexes between TiO and H₂ more than molecular H₂TiO. At the CASSCF(10/10) level, both bent and planar structures were located in both ³A′ and ³A″ states, while only the bent structure is found on the ³A″ surface when the larger (10/11) active space is used. On the basis of the vibrational analyses at the CASSCF(10/11) level of theory, the planar structure in the ³A′ state is a transition structure connecting two equivalent bent structures. The bent structure is more stable by 10 kcal/mol in the ³A″ state than that in the ³A′ state at the CASSCF(10/11) level. However, these bent structures are unstable to distortions along the asymmetric mode of the two H₂ hydrogen atoms. Reoptimization of the bent structures without symmetry constraint results in dissociation of the bent structure to TiO and H₂. Therefore, we conclude that the lowest triplet state of titanone is not bound, but rather a dissociative state relative to triplet TiO + H₂.

Hydroxysilylene (HSiOH), the divalent isomer of silanone, is known to be competitive in stability with silanone.[22,23] At the CCSD(T)/6-311++G(2df,2pd) level of theory, HSiOH is virtually isoenergetic with H₂SiO.[23] Therefore, it is of interest to determine the relative energies of titanone and its divalent isomer HTiOH. HTiOH has a linear structure in all states investigated at all levels of theory used in this work (See Table 4). Note that the geometry optimizations were started from bent structures with C_s symmetry. As in the case of linear TiH₂, the lowest triplet electronic states (³A′ and ³A″), corresponding to the degenerate ³Δ state, are derived from one electron excitations from the δ 3d orbitals ($d_{x^2-y^2}$ and d_{xy}) to the σ 3d (d_{z^2}) orbital, where z is the molecular axis. The bond distances in the triplet states do not change if state averaged CASSCF-(10/11) calculations including both δ 3d orbitals are used for the geometry optimization. The bond distances are quite similar in all three (closed shell singlet and two triplet) states.

It was shown previously that the simplest divalent titanium species, TiH₂,[24] has a bent structure with an exceedingly flat potential energy surface, so flat that minor changes in the level of theory or basis set used affects the prediction of linearity or
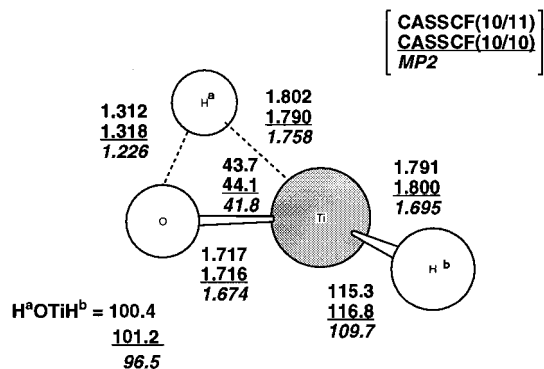

Figure 1. The calculated transition structure for reaction 0 at the three levels of theory. Bond lengths are given in angstroms, bond angles in degrees.

TABLE 6: Energetics (kcal/mol) for the Isomerization of HTiOH to H₂TiO. All Energies Are Given Relative to Singlet H₂TiO

level	transition structure	HTiOH
RHF	46.6	−29.6
CASSCF(10/10)	49.2	13.9
CASSCF(10/11)	45.2	17.7
MP2	65.1	44.0
MP4SDTQ[a]	65.2	50.3
QCISD[a]	43.5	21.2
CCSD[a]	37.7	10.9
QCISD(T)[a]	40.5	18.6
CCSD(T)[a]	42.6	19.1
CASPT2[b]	46.0	22.4
+ ZPC[c]	45.4	25.1

[a] Single point energies at the CASSCF(10/10)/TZVP geometries. [b] Single point energies at the CASSCF(10/11)/TZVP geometries. [c] The CASPT2 energies corrected by CASSCF zero point energies.

nonlinearity. The inclination to bend was sensitive, in particular, to the inclusion of Ti 4p orbitals in the CASSCF active space. It is possible that adding 4p orbitals to the HTiOH active space will also result in a slightly bent structure, but this is not expected to alter any of the conclusions drawn here.

The CASSCF relative energies of HTiOH in the singlet and triplet states are summarized in Table 5. Note that the relative energies predicted by the two different active spaces are quite similar. The ground state of titanone is clearly the closed shell ¹A′ state, while that of the HTiOH divalent isomer is the doubly degenerate ³A′, ³A″ (³Δ) state. The HTiOH triplet states are 24.5 and 18.0 kcal/mol below the ¹A′ state at the CASSCF(10/11) and CASPT2 levels of theory, respectively. In contrast, the metastable triplet state of titanone is predicted to lie higher than the ground singlet state by more than 42.5 kcal/mol.

1,2-Hydrogen Transfer Reaction between H₂TiO and HTiOH. H₂TiO and HTiOH can isomerize to each other by a 1,2-hydrogen transfer, as illustrated in reaction 0, Scheme 1. The structure of the transition state and the relative energies of the reaction in the singlet state are presented in Figure 1 and Table 6, respectively. The relative energies of H₂TiO and HTiOH are highly dependent on the level of theory, as shown in Table 6. Correlation is clearly essential, as Hartree−Fock incorrectly predicts HTiOH to be the lower energy isomer. It is also clear that the HTiOH part of the potential energy surface is strongly multireference in nature. This may be seen from the very large differences in energetic predictions by MP2 and MP4, on one hand, and CASSCF, CASPT2, and CCSD(T) on the other hand. The very large differences between the predictions of CCSD vs QCISD and nontrivial differences between QCISD(T) and CCSD(T) are also indicators of multireference character. One
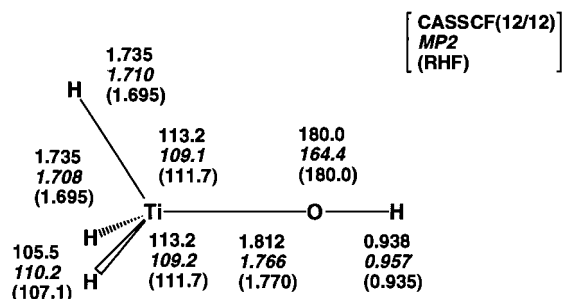
Figure 2. The calculated structure of TiH$_3$OH at three levels of theory. Bond lengths are given in angstroms, bond angles in degrees.

may examine the CASSCF natural orbital occupation numbers (NOON) in the two isomers and the transition state to assess the multireference character. The largest NOON values in the occupied and unoccupied orbitals in active spaces are 1.922 (π_{Ti-O}), 0.074 ($\pi_{Ti-O}*$) in titanone, 1.862 (σ_{Ti-O}), 0.148 ($\pi_{Ti-O}'*$) in the transition state, and 0.628 (δ), 0.744 (σ type 3d$_{Ti}$) in HTiOH. A purely closed shell species would have 2.0 electrons in the bonding ("occupied") orbitals and 0.0 electrons in the antibonding ("unoccupied") orbitals. The deviations from these values become larger in the order titanone < transition state < HTiOH. The large values in HTiOH illustrate the multireference character of the $^1\Sigma^+$ state as in the $^1\Sigma_g^+$ state of linear TiH$_2$.[24] This would cause a larger dependence of the reaction energy than the barrier height on the level of theory used.

The best estimate for the barrier height is ≈45 kcal/mol (25 kcal/mol from the HTiOH direction), and H$_2$TiO is predicted to be the lower energy isomer by about 20 kcal/mol, on the singlet potential energy surface. Of course, the ground state of HTiOH is a triplet (Table 5), 18 kcal/mol more stable than singlet at the CASPT2 level of theory. Therefore, in the singlet state, isomerization of H$_2$TiO to HTiOH will be very difficult at room temperature. However, in the triplet state, the isomerization of metastable H$_2$TiO to HTiOH should occur with little or no barrier, since their relative stabilities are reversed. The triplet energy difference is estimated to be 38.1 kcal/mol at the CASPT2 level, based on the data in Tables 5 and 6. Of course, a competing process is decomposition of triplet H$_2$TiO to TiO + H$_2$.

B. TiH$_3$OH. *Structures.* The HF, MP2, and CASSCF(12/12) optimized structure of singlet TiH$_3$OH are displayed in Figure 2. The total CASSCF(12/12) energy is −925.75479 hartrees.

As for HTiOH, the TiOH bond angle in TiH$_3$OH is predicted to be completely linear both at the HF and the CASSCF(12/12) levels. On the other hand, the MP2 TiOH bond angle is slightly bent. In any case, TiH$_3$OH has a very large TiOH bond angle, in contrast with the XOH angles in SiH$_3$OH and CH$_3$-OH. This is very likely related to strong back-bonding from the oxygen lone pairs into the empty Ti d orbitals. The CASSCF Ti−O and Ti−H bond distances are the longest among the three levels of theory, suggesting that there is significant mixing of antibonding character into the bonds at the CASSCF(12/12) level. The Ti−O bond length of 1.812 Å is in reasonable agreement with the experimental values (1.8−2.0 Å) for the Ti−O single bond.[3]

Decomposition Reactions. To assess the stability of TiH$_3$-OH to unimolecular decomposition, we have considered several decomposition paths in the ground singlet state (See Scheme 1 for reactions and reaction numbers). The schematic potential energy surface is shown in Figure 3.
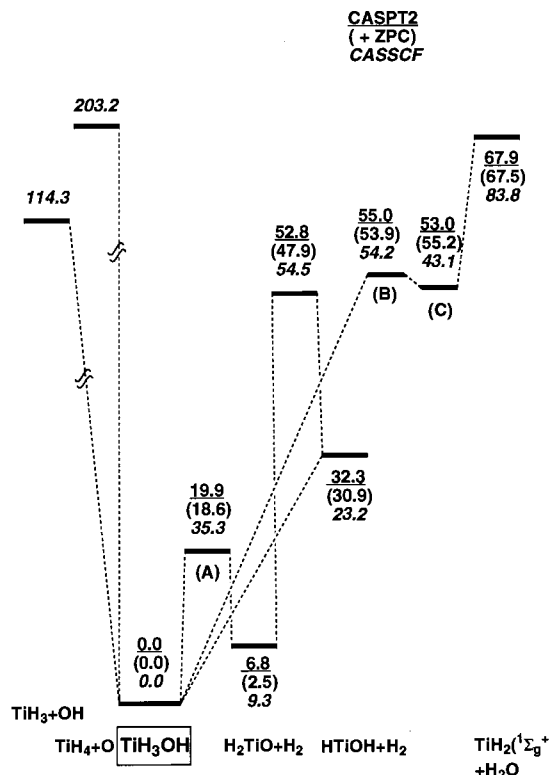

Figure 3. The potential energy surface for the decomposition reaction of TiH$_3$OH at the CASPT2(12/13)//CASSCF(12/12) and CASSCF(12/12) levels. The barrier height for reaction 0 is estimated at the CASPT2-(10/11)//CASSCF(10/11) and CASSCF(10/11) levels. See Figure 4 for **A** − **C**.

The structures labeled **A** and **B** in Figure 4 are the CASSCF-(12/12) transition state structures for reactions 1 and 3, the elimination of H$_2$ and H$_2$O, respectively. Structure **A** has C_s symmetry while **B** has C_1 symmetry. These structures correspond to CASPT2 barrier heights of 20 and 55 kcal/mol, respectively (Figure 3). Furthermore, the intermediate complex **C** was located between the transition structure **B** and the decomposition products TiH$_2$ + H$_2$O on the potential energy surface of reaction 3. In this structure, the molecular planes of TiH$_2$ and H$_2$O are perpendicular with each other. This intermediate complex is more stable than **B** and products by 2 and 14.9 kcal/mol, respectively, at the CASPT2 level, and is analogous to the SiH$_2$:OH$_2$ complex found on the single SiH$_3$-OH potential energy surface.[25]

A transition structure for reaction 2 was located at the HF level of theory. However, several attempts to locate the analogous transition state with CASSCF wave functions with alternative starting points were unsuccessful. Figure 5 illustrates a series of CASSCF(6/6) partial optimizations and CASSCF-(12/12) single point energies in which the two Ti−H bond lengths are fixed and the remaining geometric parameters optimized. The overwhelming evidence is that this decomposition of TiH$_3$OH to HTiOH + H$_2$ proceeds with a monotonic increase of energy. No attempt has been made to locate the transition structures for reactions 4 and 5,[26] because both of these reactions are found to be highly endothermic (see Figure 3).

TiH$_2$ is predicted to be linear at the CASSCF(6/7) level of theory, although, as noted above, it is found to be very slightly bent when larger active spaces and dynamic correlation are employed. The estimated Ti−H bond length of 1.910 Å in the present study is in good agreement with the value of 1.899 Å found for TiH$_2$ in the $^1A_1$ obtained at the SA-CASSCF(6/11)
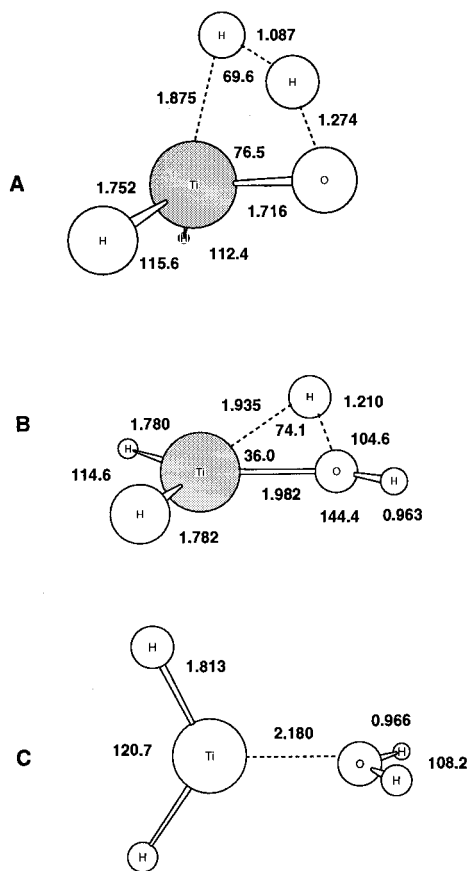
Figure 4. The CASSCF(12/12) transition structure for reaction 1 (**A**) and reaction 3 (**B**), and the intermediate complex of reaction 3 (**C**). Bond lengths are given in angstroms, bond angles in degrees.
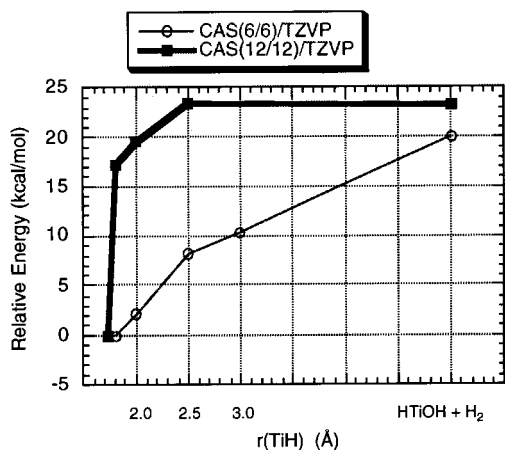

Figure 5. The potential energy surface of reaction 2, TiH$_3$OH $\rightarrow$ HTiOH + H$_2$ calculated at the CASSCF(6/6) and CASSCF(12/12)// CASSCF(6/6) levels.

level.[24] The linear structure is used for the discussion of energetics, because the small energy difference between the linear and bent structures is not significant. The optimized structure of TiH$_3$ converged to planar D_{3h} from a nonplanar C_{3v} starting geometry. The singly occupied molecular orbital (SOMO) is mainly constructed from the d$_{z^2}$ orbital perpendicular to the molecular plane. For TiH$_4$, the CASSCF (8/9) Ti–H bond length of 1.738 Å is slightly longer than the MP2 value of 1.70 Å.[27]

The CASSCF(12/12) and CASPT2(12/13)//CASSCF(12/12) potential energy surfaces for the ground singlet state TiH$_3$OH unimolecular decomposition reactions are summarized in Figure

3. All Ti 3d orbitals are included in the CASPT2(12/13) active space. Reactions 1 and 2 are related to the H$_2$TiO $\leftrightarrow$ HTiOH isomerization reaction (reaction in Scheme 1) discussed above. TiH$_3$OH is thermodynamically lowest in energy among all of the stationary points considered. The barrier heights for the decomposition reactions increase in the order (1) < (2) < (3). Since reactions 4 and 5 are so endothermic, their transition states, if they exist, have not been explored. Also, the potential energy increases monotonically along the decomposition path to HTiOH and H$_2$, as noted above. Therefore, on the basis of the sizable energy barriers, TiH$_3$OH is predicted to be kinetically stable to unimolecular decomposition and should be experimentally observable. It should be recalled in this regard that the ground states of HTiOH and TiH$_2$ are triplets. Therefore, it is possible that as singlet TiH$_3$OH dissociates to one of these products, an intersystem crossing induced by spin–orbit coupling may occur. However, because the HTiOH and TiH$_2$ triplets are only on the order of 20 kcal/mol lower in energy than their corresponding singlets, TiH$_3$OH is still expected to be stable with respect to unimolecular decomposition (see Figure 3). Finally, note that it has been predicted previously that TiH$_4$ dimerizes with no barrier to Ti$_2$H$_8$.[27] Therefore, it is possible that TiH$_3$OH can dimerize to a bridge structure that is analogous to those found for Ti$_2$H$_8$.[27,28]

It is interesting to compare the calculations presented here with analogous calculations on silanol (SiH$_3$OH),[29] because Si and Ti have somewhat similar electronic configurations (s^{2}p^2 vs s^{2}d^2). Although the silanol calculations were performed at a different level of theory (fourth-order perturbation theory with the 6-311G(d,p) basis set), qualitative comparisons are still useful. The Si–O and Ti–O bond energies are predicted to be quite similar, as measured by the dissociation to MH$_3$ + OH: 117 kcal/mol for M = Si vs 114 kcal/mol for M = Ti. For Si, the 1,2-elimination of H$_2$ is predicted to be endothermic by 44 kcal/mol with a 71 kcal/mol barrier. The analogous values for Ti (Figure 3) are 7 and 20 kcal/mol. Therefore, this is a much more facile process for Ti. Elimination of water from silanol to yield singlet silylene is endothermic by 72 kcal/mol with a barrier of 80 kcal/mol. Elimination of water from TiH$_3$OH is endothermic by 68 kcal/mol (very similar to that for silanol) with no net intervening barrier. Finally, HSiOH and H$_2$SiO were predicted to be nearly isoenergetic, with the latter slightly lower in energy, while H$_2$TiO is predicted here to be more than 20 kcal/mol lower in energy than HTiOH. This latter comparison is clearly related to the relative ease of the 1,2-H$_2$ elimination.

IV. Summary and Conclusions

In an attempt to explore the nature of Ti–O doubly and singly bonded compounds, we have carried out ab initio molecular orbital calculations for unimolecular thermal decomposition mechanisms of TiH$_3$OH, as well as an analysis of the molecular and electronic structure of one of the key decomposition products, H$_2$TiO. Titanone (H$_2$TiO) has a nonplanar structure in the ground singlet state. The Ti=O double bond is predicted to be very polar based on population analyses. The doubly bonded species is predicted to be more stable than its linear divalent Ti isomer HTiOH in the ground singlet state. These two isomers are separated by a sizable barrier, therefore, they are not likely to isomerize to each other by a 1,2-hydrogen transfer at room temperature. On the triplet sate potential energy surface, low-lying H$_2$TiO states within C_s symmetry are much higher in energy than the singlet (42.5 kcal/mol at the CASPT2) and appear to be unstable to dissociation to TiO + H$_2$. On the

other hand, HTiOH has a triplet ground state: the $^3\Delta$ state of HTiOH is 18 kcal/mol more stable than the $^1\Sigma^+$ state.

TiH$_3$OH is predicted to be the global minimum on its ground state potential energy surface, and predicted barriers to unimolecular decomposition are at least 20 kcal/mol. Therefore, this molecule is predicted to be kinetically stable to the various unimolecular decomposition reactions to fragment molecules such as H$_2$TiO, HTiOH, TiH$_2$, TiH$_3$, and TiH$_4$ in the ground singlet state. However, it is possible that TiH$_3$OH may dimerize without barrier, as other simple titanium compounds do.[27,28]

While the TiO and SiO bonds in the respective MH$_3$OH compounds are predicted to be similar, the 1,2-H$_2$ elimination is found to be much easier energetically for M = Ti.[29]

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