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Methane Activation by Titanium Monoxide Molecules: A Matrix Isolation Infrared Spectroscopic and Theoretical Study

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Abstract: Reactions of titanium monoxides with methane have been investigated using matrix isolation infrared spectroscopy and theoretical calculations. Titanium derivatives of several simple oxyhydrocarbons have been prepared and identified. The titanium monoxide molecules prepared by laser evaporation of bulk TiO_2 target reacted with methane to form the $TiO(CH_4)$ complex in solid argon, which was predicted to have C_{3v} symmetry with the oxygen atom coordinated to one hydrogen atom of the methane molecule. The complex rearranged to the $CH_3Ti(O)H$ titano−acetaldehyde molecule upon visible ($\lambda > 500$ nm) irradiation. The titano−acetaldehyde molecule sustained further photochemical rearrangement to the CH_2-Ti(H)OH titano−vinyl alcohol molecule, which was characterized to be a simple carbene complex involving agostic bonding. The $CH_2Ti(H)OH$ molecule reacted with a second methane to form the $(CH_3)_2Ti(H)OH$ titano−isopropyl alcohol molecule spontaneously on annealing. The $(CH_3)_2Ti(H)OH$ molecule also can be produced via UV photon-induced rearrangement of the $CH_3Ti(O)H(CH_4)$ complex.

Introduction

The selective transformation of ubiquitous but inert C−H bonds of alkanes such as methane to other functional groups is of great economic and scientific importance. Many examples of C−H bond activation at transition-metal centers have been reported.[1−4] To develop practical alkane conversion processes, much remains to be learned about the processes and factors controlling the activity and selectivity of catalytic alkane activation. Reactions of transition-metal atoms and simple metal oxides with methane serve as the simplest model in understanding the intrinsic mechanism of the catalytic alkane conversion processes.

Previous investigations on reactions between transition-metal atoms and methane have shown that insertion into the C−H bond of methane is more facile for metal cations than for neutral metal atoms.[5−10] Transition-metal cations such as zirconium, tantalum, iridium, and platinum all reacted with methane at thermal energies, whereas only neutral platinum atom activated the C−H bond of methane from a gas-phase kinetics study.[10] Theoretical and matrix isolation experimental investigations suggested that only the neutral rhodium atom is able to activate the C−H bond of methane.[11,12] All of the other transition-metal atoms either are unreactive toward methane or undergo oxidative insertion to form the $HMCH_3$ species when the metal atom is electronically excited in low-temperature matrixes.[13−17] Recent investigations also showed that the $HMCH_3$ molecules can undergo further photon-induced rearrangement to form the agostic $CH_2{=}MH_2$ methylidene complexes (group IV metals)[18−20] and $CH{\equiv}MH_3$ methylidyne molecules (Mo and W).[21]

The reactivity of simple transition-metal oxide cations such as monoxide and dioxide cations with methane also has been widely studied in the gas phase.[22−30] The results indicated that

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late transition-metal monoxide ions of the first row can efficiently convert methane to methanol, while the early transition-metal monoxide ions cannot; most dioxide cations are found to be more reactive than the corresponding bare metal cations and monoxide cations. By contrast, reactions of neutral transition-metal oxides with methane have received much less attention. Some theoretical calculations on methane activation by neutral transition-metal oxide molecules ScO, NiO, PdO, and MO_x (M = Cr, Mo, W, and $x = 1-3$) have been reported,[31,32] which have provided valuable information concerning the reaction mechanism and energetics. More recently, reactions of monoxides such as FeO, MnO, NbO, and TaO with methane have been investigated in this laboratory using matrix isolation infrared absorption spectroscopy as well as theoretical calculations.[33,34] It was found that the monoxide molecules reacted with methane to form the weakly bound complexes, which underwent photon-induced rearrangement to the CH_3-MOH (M = Fe, Mn) or $CH_3M(O)H$ (M = Nb, Ta) molecules. In this paper we report a combined matrix isolation infrared spectroscopic and theoretical study of the reaction of titanium monoxide with methane, which provides a prototype reaction in understanding the mechanism of methane activation by transition-metal oxides.

Experimental and Theoretical Methods

The experimental setup for pulsed laser evaporation and matrix isolation infrared spectroscopic investigation has been described in detail previously.[35] Briefly, the 1064 nm Nd:YAG laser fundamental (Spectra Physics, DCR 150, 20 Hz repetition rate and 8 ns pulse width) was focused onto the rotating Ti or TiO_2 target. The TiO_2 target was prepared by sintered titanium dioxide powders. The ablated species were co-deposited with reagent gas in excess argon onto a 12 K CsI window for 1−3 h at a rate of approximately 4 mmol/h. Isotopic labeled CD_4 (Isotec, 99%),$^{13}CH_4$ (Isotec, 99%), and $CH_3{}^{18}OH$ (Isotec, 99%) were used in different experiments. Infrared spectra were recorded on a Bruker IFS 113 V spectrometer at 0.5 cm^{-1} resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband irradiation using a tungsten lamp or a high-pressure mercury arc lamp with glass filters.

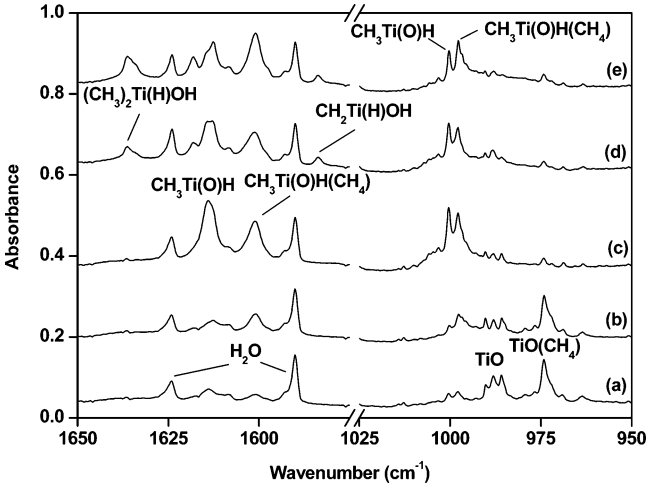

Figure 1. Infrared spectra in the 1650−1575 and 1025−950 cm^{-1} regions from co-deposition of laser-evaporated TiO with 5.0% CH_4 in argon: (a) after 3 h of sample deposition at 12 K, (b) after 30 K annealing, (c) after 30 min of $\lambda > 500$ nm irradiation, (d) after 30 min of $\lambda > 250$ nm irradiation, and (e) after 35 K annealing.

Density functional calculations were performed using the Gaussian 03 program.[36] The three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr (B3LYP) was utilized.[37] The 6-311++G(3df, 3pd) basis set was used for the H, C, Ti, and O atoms.[38] Recent studies have shown that this hybrid DFT functional with a relatively large basis set can provide a very reliable prediction for agostic bonding.[39] The geometries were fully optimized, and the stability of the electronic wave function was tested; the harmonic vibrational frequencies were calculated with analytic second derivatives, and zero-point energies (ZPE) were derived. The single-point energies of all structures optimized at the B3LYP level were calculated using the CCSD(T) method with the 6-311++G(d,p) basis sets.[40]

Results and Discussion

Infrared Spectra. The titanium monoxide reactant was prepared from pulsed laser evaporation of bulk TiO_2 target. Under controlled laser energy, co-condensation of the species from laser evaporation of TiO_2 with pure argon at 12 K produced strong titanium monoxide (990.3, 988.1, and 985.7 cm^{-1}) and dioxide absorptions ($^{48}TiO_2$: ν_1, 917.0 cm^{-1} and ν_3, 946.9 cm^{-1}).[41] These absorptions showed no obvious change upon annealing and broadband irradiation. Distinct new product absorptions were observed in the experiments when different concentration CH_4/Ar mixtures (ranging from 0.2% to 5%) were used as the reagent gas. Figures 1 and 2 show the representative spectra in selected regions with a CH_4/Ar sample (5.0% molar ratio), and the product absorptions are listed in Table 1. Besides the aforementioned titanium oxide absorptions, new absorptions at 974.1 and 1285.8 cm^{-1} were observed after sample deposition at 12 K. These absorptions disappeared when the matrix was irradiated by the output of a tungsten lamp with a $\lambda > 500$ nm

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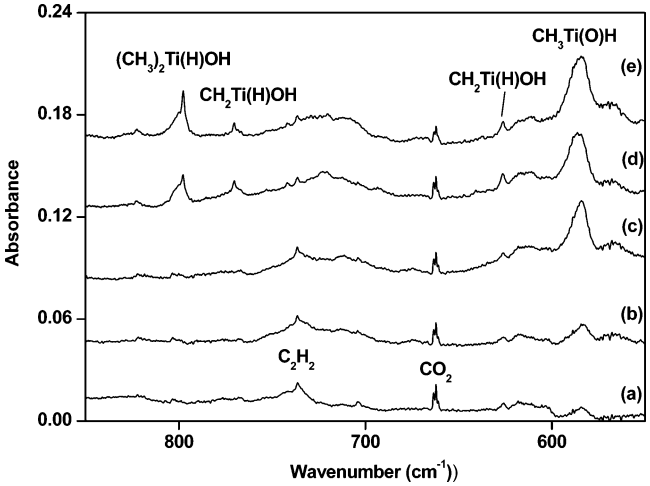

Figure 2. Infrared spectra in the 850−550 cm^{-1} region from co-deposition of laser-evaporated TiO with 5.0% CH_4 in argon: (a) after 3 h of sample deposition at 12 K, (b) after 30 K annealing, (c) after 30 min of $\lambda > 500$ nm irradiation, (d) after 30 min of $\lambda > 250$ nm irradiation, and (e) after 35 K annealing.

pass filter ($500 < \lambda < 1000$ nm), during which absorptions at 1613.9, 1600.9, 1000.4, 997.9, 583.7, and 474.7 cm^{-1} were produced. Additional irradiation with the mercury arc lamp without filter ($250 < \lambda < 580$ nm) decreased the 1613.9, 1600.9, 1000.4, 997.9, 583.7, and 474.7 cm^{-1} absorptions and produced new absorptions at 3749.0, 3726.7, 1635.8, 1583.8, 797.8, 770.4, and 626.2 cm^{-1}. The 3726.7, 1613.9, 1583.8, 1000.4, 770.4, and 626.2 cm^{-1} absorptions decreased, whereas the 3749.0, 1635.8, 1600.9, 997.9, and 797.8 cm^{-1} absorptions increased upon sample annealing to 35 K. The experiments were repeated with the isotopic labeled CD_4, $^{13}CH_4$, and $^{12}CH_4 + {}^{13}CH_4$ samples to help with product identification. The isotopic frequencies are also listed in Table 1. Infrared spectra in selected regions using different isotopic samples are shown in Figures 3 and 4.

Several experiments were done by depositing methanol in argon (0.2%) with laser-evaporated titanium atoms. The spectra in the 1635−1575 and 1050−950 cm^{-1} regions are shown in Figure 5. The 1613.9, 1583.8, and 1000.4 cm^{-1} absorptions were produced upon $300 < \lambda < 580$ nm irradiation. The 1583.8 cm^{-1} band increased whereas the 1613.9 and 1000.4 cm^{-1} bands decreased on $250 < \lambda < 580$ nm irradiation. The 1583.8 cm^{-1} band exhibited no shift, while the 1613.9 and 1000.4 cm^{-1} absorptions were shifted to 1613.2 and 959.3 cm^{-1} with the $CH_3{}^{18}OH$ sample (Figure 5, trace d).

$TiO(CH_4)$. The 974.1 cm^{-1} absorption, which shows no carbon-13 isotopic shift and a small (6.4 cm^{-1}) deuterium shift, is assigned to the $TiO(CH_4)$ complex. This absorption is barely observed in the experiment when laser-evaporated titanium atoms were co-deposited with O_2/CH_4 mixture, in which the TiO absorption is very weak. The band position also suggests that it is due to the Ti−O stretching mode of a TiO complex. The very weak absorption at 1285.8 cm^{-1} is the CH_2 deformation mode of the complex, which shows about the same isotopic frequency shift as that of CH_4 observed at 1305.4 cm^{-1}. The $TiO(CH_4)$ complex was predicted to have a C_{3v} structure with one H atom of CH_4 coordinated to the O atom of TiO (Figure 6). The small deformation of the CH_4 and TiO subunits and the rather long O−H distance (2.658 Å) indicate weak interaction between the CH_4 and TiO subunits. The binding energy with respect to $TiO + CH_4$ was predicted to be 1.1 kcal/mol at the CCSD(T) level, significantly lower than those of other previously reported transition-metal monoxide−methane complexes, which were predicted to be coordinated between the metal and H atoms.[31−34]

$CH_3Ti(O)H$ and $CH_3Ti(O)H(CH_4)$. The absorptions at 1613.9 and 1000.4 cm^{-1} appeared under $500 < \lambda < 1000$ nm irradiation at the expense of the $TiO(CH_4)$ absorptions. This observation suggests that the 1613.9 and 1000.4 cm^{-1} absorptions are most likely due to a structural isomer of $TiO(CH_4)$. The same absorptions were also observed in the $Ti + CH_3OH$ experiments. The 1613.9 cm^{-1} absorption shows no shift with the $^{13}CH_4$ sample and shifted to 1165.3 cm^{-1} with the CD_4 sample. The band position and the H/D isotope frequency ratio (1.3850) are characteristic of a Ti−H stretching vibration.[42] The absorption at 1000.4 cm^{-1} exhibits a very small (0.3 cm^{-1}) carbon-13 shift and large oxygen-18 (41.1 cm^{-1}) shift. The band position and $^{16}O/^{18}O$ isotopic frequency ratio (1.0428) indicate a terminal Ti−O stretching vibration. Accordingly, we assign the 1613.9 and 1000.4 cm^{-1} absorptions to the $CH_3Ti(O)H$ molecule. These frequencies are comparable to the 1611.9 (antisymmetric Ti−H stretch) and 1010.5 cm^{-1} (Ti−O stretch) values for the tetravalent Ti species H_2TiO observed in solid argon.[43]

The absorptions at 1600.9 and 997.9 cm^{-1} are several wavenumbers red shifted from the Ti−H and Ti−O stretching modes of $CH_3Ti(O)H$. The band positions and isotopic frequency shifts indicate that the upper band is due to a Ti−H stretching mode, and the lower band is a Ti−O stretching mode. These absorptions were not observed in the $Ti + CH_3OH$ experiments. Both absorptions increased together on annealing at the expense of the $CH_3Ti(O)H$ absorptions, and the relative intensities with respect to the $CH_3Ti(O)H$ absorptions increased with increasing CH_4 concentrations. The above-mentioned observations led us to assign these absorptions to the $CH_3Ti(O)H(CH_4)$ complex.

The $CH_3Ti(O)H$ molecule was predicted to have a singlet ground state with a nonplanar C_1 structure (Figure 6). The calculated Ti−C bond length of 2.088 Å suggests a Ti−C single bond, which is very close to the standard single Ti−C bond lengths in tetraaryl compounds.[44] The $CH_3Ti(O)H$ molecule can be regarded as a titano−acetaldehyde. The Ti−H and Ti−O stretching modes were computed at 1678.0 and 1064.9 cm^{-1}, respectively. These two modes were predicted to have the largest IR intensities. The isotopic frequency shifts calculated for both modes fit the experimental values very well (Table 1). The calculations also predicted that $CH_3Ti(O)H$ may be coordinated by another CH_4 molecule to form the $CH_3Ti(O)H(CH_4)$ complex, which was computed to have η^3-CH_4 bonding, that is, the titanium atom is coordinated by three hydrogen atoms of CH_4 (Figure 6). The distance between Ti and C is 2.485 Å. The Ti−O, Ti−C, and Ti−H bond lengths of $CH_3Ti(O)H$ were slightly elongated upon CH_4 coordination, which induced a red shift of the corresponding vibrational frequencies.

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Table 1. Infrared Absorptions (cm^{-1}) from Co Deposition of Laser-Evaporated Titanium Oxides with CH_4 in Solid Argon at 12 K (calculated frequencies are also listed in parentheses for comparison)

CH_4	$^{13}CH_4$	CD_4	assignment
3749.0 (3934.1)	3749.0 (3934.1)	2782.4 (2867.4)	$(CH_3)_2Ti(H)OH$ (O−H stretch)
3726.7 (3911.5)	3726.7 (3911.5)	2759.3 (2849.4)	$CH_2Ti(H)OH$ (O−H stretch)
1635.8 (1703.5)	1635.8 (1703.5)	1183.7 (1218.8)	$(CH_3)_2Ti(H)OH$ (Ti−H stretch)
1613.9 (1678.0)	1613.9 (1678.0)	1165.3 (1200.9)	$CH_3Ti(O)H$ (Ti−H stretch)
1600.9 (1659.0)	1600.9 (1658.9)	1155.9 (1187.3)	$CH_3Ti(O)H(CH_4)$ (Ti−H stretch)
1583.8 (1648.7)	1583.8 (1648.7)	1144.6 (1180.2)	$CH_2Ti(H)OH$ (Ti−H stretch)
1285.8 (1334.1)	1278.3 (1325.9)		$TiO(CH_4)$ (CH_2 deformation)
1000.4 (1064.9)	1000.1 (1064.6)		$CH_3Ti(O)H$ (Ti−O stretch)
997.9 (1049.8)	997.6 (1049.6)		$CH_3Ti(O)H(CH_4)$ (Ti−O stretch)
974.1 (1039.2)	974.1 (1039.2)	967.7 (1039.3)	$TiO(CH_4)$ (Ti−O stretch)
797.8 (796.5)	797.4 (796.2)	772.9 (768.8)	$(CH_3)_2Ti(H)OH$ (Ti−OH stretch)
770.4 (761.2)	765.9 (755.6)	733.7 (710.1)	$CH_2Ti(H)OH$ (Ti−OH stretch)
626.2 (669.9)	618.3 (664.0)		$CH_2Ti(H)OH$ (CH_2 wagging)
583.7 (597.7)	580.3 (595.0)	501.8 (515.6)	$CH_3Ti(O)H$ (HTiO bend + TiC stretch)
583.7 (598.6)	580.3 (596.7)	511.5 (509.1)	$CH_3Ti(O)H(CH_4)$ (HTiO bend+TiC stretch)
474.7 (496.2)		436.3 (447.2)	$CH_3Ti(O)H$ (HTiO deformation)

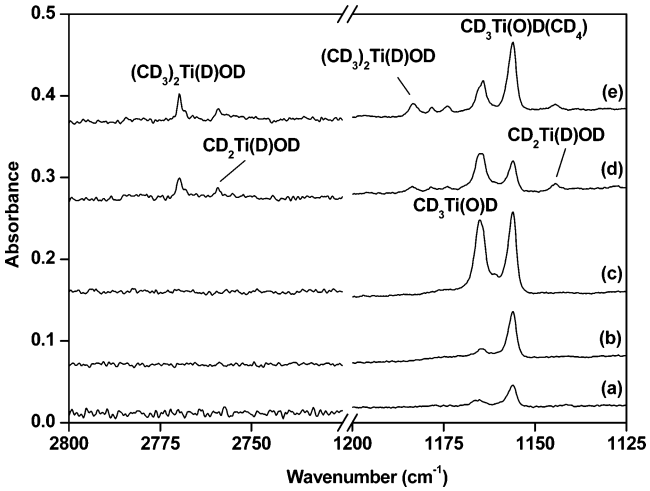

Figure 3. Infrared spectra in the 2800−2725 and 1200−1125 cm^{-1} regions from co-deposition of laser-evaporated TiO with 5.0% CD_4 in argon: (a) after 3 h of sample deposition at 12 K, (b) after 30 K annealing, (c) after 30 min of $\lambda > 500$ nm irradiation, (d) after 30 min of $\lambda > 250$ nm irradiation, and (e) after 35 K annealing.

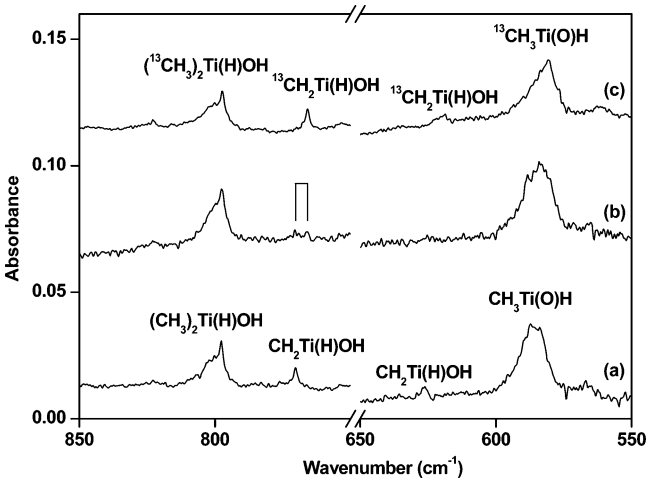

Figure 4. Infrared spectra in the 850−750 and 650−550 cm^{-1} regions from co-deposition of laser-evaporated TiO with methane in excess argon. Spectra were taken after 3 h of sample deposition followed by 30 min of $\lambda > 250$ nm irradiation: (a) 2.0% $^{12}CH_4$, (b) 2.0% $^{12}CH_4$ + 2.0% $^{13}CH_4$, and (c) 2.0% $^{13}CH_4$.

Weak absorption at 474.7 cm^{-1} exhibited the same annealing and photolysis behavior as the 1613.9 and 1000.4 cm^{-1} absorptions and is assigned to the HTiO deformation mode of $CH_3Ti(O)H$, which was predicted at 496.2 cm^{-1}. A broad band centered at 583.7 cm^{-1} tracked with the sum of the 1613.9 and 1600.9 cm^{-1} absorptions. This band is assigned to the mixed HTiO bending and Ti−C stretching mode of $CH_3Ti(O)H$ and $CH_3Ti(O)H(CH_4)$, which were predicted at 597.7 cm^{-1} for CH_3-Ti(O)H and 598.6 cm^{-1} for $CH_3Ti(O)H(CH_4)$.

$CH_2Ti(H)OH$. Weak absorptions at 3726.7, 1583.8, 770.4, and 626.2 cm^{-1} appeared together on $250 < \lambda < 580$ nm irradiation, during which the $CH_3Ti(O)H$ absorptions decreased. The 3726.7 cm^{-1} absorption is due to an O−H stretching mode, which shifted to 2759.3 cm^{-1} with CD_4 (H/D ratio 1.3506). The 1583.8 cm^{-1} absorption exhibited an H/D isotopic ratio of 1.3837 and is a Ti−H stretching vibration. The 770.4 cm^{-1} absorption is largely a Ti−OH stretching mode but with some carbon involvement. It shifted to 765.9 cm^{-1} with $^{13}CH_4$, and only the pure isotopic counterparts were observed in the experiment with a mixed $^{12}CH_4$ + $^{13}CH_4$ sample (Figure 4). The 626.2 cm^{-1} absorption shifted to 618.3 cm^{-1} with $^{13}CH_4$ and is due to a CH_2 wagging vibration. Accordingly, we assign these absorptions to the $CH_2Ti(H)OH$ molecule.

Our calculations predicted that the $CH_2Ti(H)OH$ molecule has a singlet ground state with nonplanar C_1 structure, as illustrated in Figure 6. The Ti−C bond length of 1.815 Å is slightly shorter than the experimentally known Ti=C double bond length.[45] The $CH_2Ti(H)OH$ molecule is a methylidene hydrido hydroxide complex, which can also be regarded as a titano−vinyl alcohol molecule. Similar to the recently reported methylidene hydride $CH_2{=}MH_2$ and the fluorine-substituted derivatives $CH_2{=}MHF$ (M = Ti, Zr, Hf, Mo, and W),[18−21,46] the $CH_2Ti(H)OH$ titano−vinyl alcohol molecule also involves agostic interaction between the metal atom and one of the α-hydrogen atoms.[47] As shown in Figure 6, the methylene group is distorted with one of the methylene hydrogen atoms located close to the Ti atom: $\angle HCTi = 89.1°$ and $r_{CH\cdots Ti} = 2.117$ Å.

(45) (a) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
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(47) Scherer, W.; McGrady, G. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1782 and references therein.

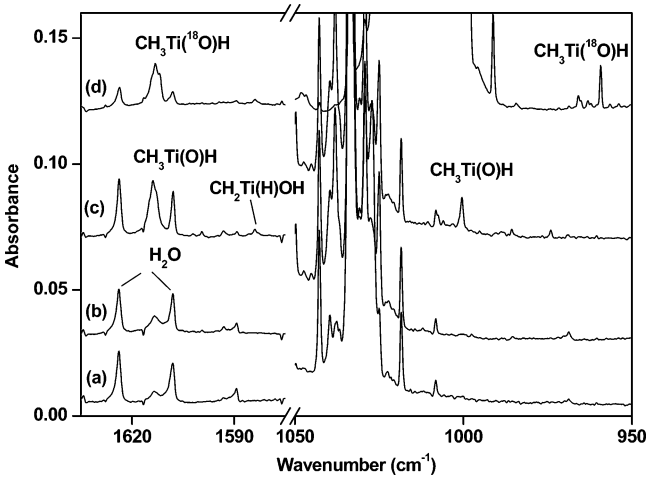


Figure 5. Infrared spectra in the 1635−1575 and 1050−950 cm^{-1} regions from co-deposition of laser-evaporated titanium with CH_3OH in excess argon: (a) 0.2% CH_3OH, 2 h of sample deposition at 12 K, (b) after 25 K annealing of sample a, (c) after 30 min of $300 < \lambda < 580$ nm irradiation of sample b, and (d) 0.2% $CH_3{}^{18}OH$, after 30 min of $300 < \lambda < 580$ nm irradiation.

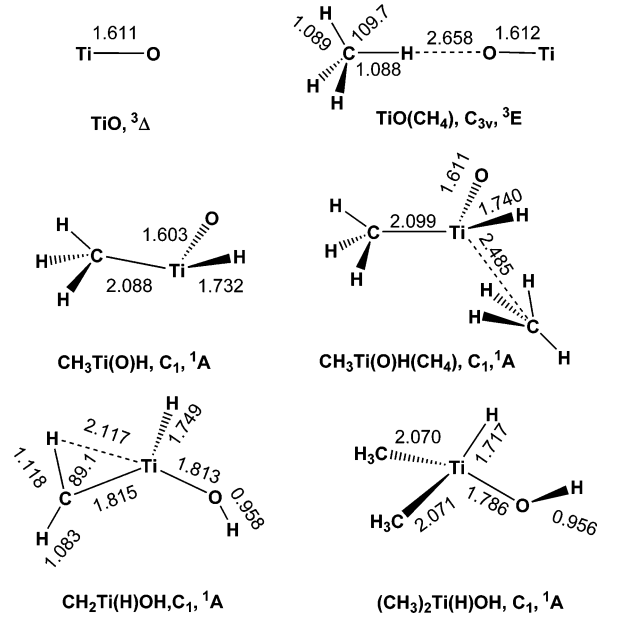
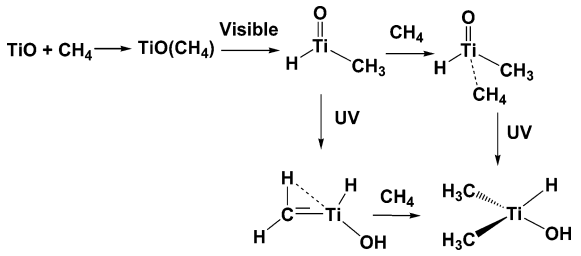


Figure 6. Optimized structures (bond lengths in angstroms, bond angles in degrees) of the observed product molecules at the B3LYP/6-311++G-(3df,3pd) level of theory.

The experimentally observed vibrational modes were computed at 3911.5, 1648.7, 761.2, and 669.9 cm^{-1} with the calculated isotopic shifts in good agreement with the experimental values.

$(CH_3)_2Ti(H)OH$. Absorptions at 3749.0, 1635.8, and 797.8 cm^{-1} appeared only upon $250 < \lambda < 580$ nm irradiation and increased on subsequent annealing. High reagent concentration favors production of these absorptions, which suggests involvement of more than one CH_4. The 3749.0 cm^{-1} absorption moved to 2782.4 cm^{-1} with the CD_4 sample and is assigned to an O−H stretching vibration. The 1635.8 cm^{-1} absorption is a Ti−H stretching vibration based upon the observed H/D isotopic frequency ratio of 1.3819. The 797.8 cm^{-1} absorption shows an isotopic shift of 0.4 cm^{-1} on carbon-13 substitution and a 24.9 cm^{-1} shift on CD_4 substitution. On the basis of the small carbon and deuterium isotopic shifts, the 797.8 cm^{-1} absorption arises from a vibrational mode such as a Ti−OH stretch where the O atom is heavily involved. The above considerations suggest the assignment of the 3749.0, 1635.8, and 797.8 cm^{-1} absorptions to the $(CH_3)_2Ti(H)OH$ titano−isopropyl alcohol molecule. Calculations were performed for the $(CH_3)_2Ti(H)$-OH molecule, which was predicted to have a singlet ground state without symmetry (C_1, see Figure 6). The H atom of the hydroxyl group tilted from the HTiO plane with a dihedral angle of 103.0°. The two Ti−C bonds are slightly different with both bond lengths close to that of $CH_3Ti(O)H$. The O−H, Ti−H, and Ti−O stretching modes were predicted to have the largest IR intensities, which absorbed at 3934.1, 1703.5, and 796.5 cm^{-1}, respectively.

Scheme 1



Reaction Mechanism. The behavior of the new product absorptions leads us to propose the reactions shown in Scheme 1.

The initial step of the TiO + CH_4 reaction is formation of the $TiO(CH_4)$ complex. From the complex one hydrogen atom of methane transferred to the metal center to form the CH_3Ti-(O)H titano−acetaldehyde molecule. According to the calculations, the singlet ground-state $CH_3Ti(O)H$ molecule is 6.9 kcal/mol lower in energy than the triplet-state $TiO(CH_4)$ complex. The H-atom transfer process is exothermic but requires activation energy. The barrier height was computed to be 23.3 kcal/mol (Figure 7). This process involves spin crossing and proceeds only under visible light ($\lambda > 500$ nm) irradiation, during which some excited states may be involved. Another possible reaction channel with hydrogen being transferred to the O atom of TiO to form the CH_3TiOH isomer was predicted to be energetically unfavorable. The CH_3TiOH isomer has a triplet ground state, which is 3.7 kcal/mol less stable than the singlet ground-state $CH_3Ti(O)H$ molecule. No evidence was found for formation of CH_3TiOH in the present experiments. This reaction feature is very similar to those of other early transition metals (Nb and Ta) but is quite different from those of late transition metals (Mn and Fe) as reported previously by our group.[33,34] The MnO-(CH_4) and $FeO(CH_4)$ complexes underwent photochemical rearrangement to form the CH_3MnOH and CH_3FeOH molecules instead of $CH_3Mn(O)H$ and $CH_3Fe(O)H$ upon UV irradiation.[33] The different reactivity can be rationalized in terms of changes in the strength of the M−O bonds and the electron count. In general, the bonds of early transition-metal monoxides are stronger than those of late transition-metal monoxides (the bond dissociation energies of TiO, MnO, and FeO are 6.92 ± 0.10, 3.83 ± 0.08, and 4.17 ± 0.08 eV, respectively).[48] The valence d electrons of early transition metals are inclined to participate in bonding to form high-valent compounds, whereas the late

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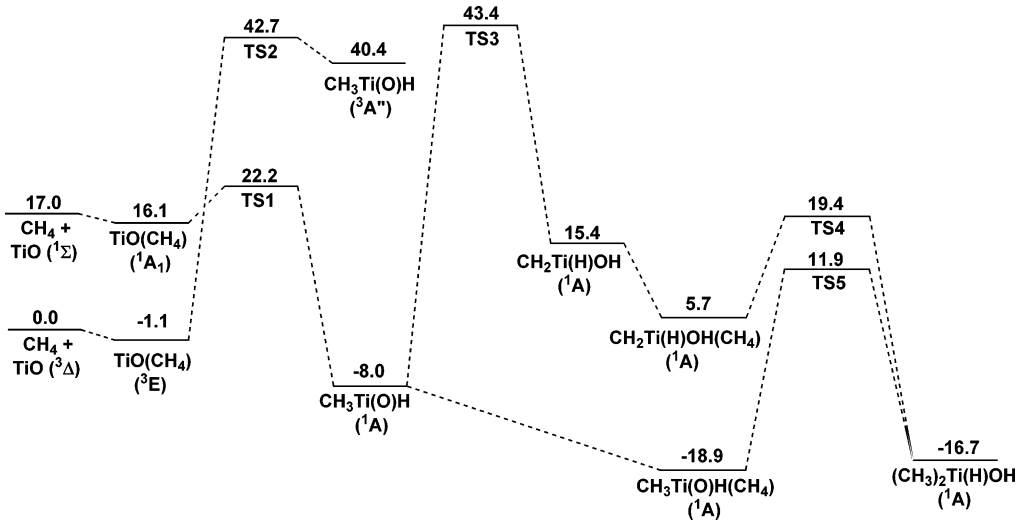

Figure 7. Potential-energy profiles for the TiO + CH_4 reaction calculated at the CCSD(T)/6-311++G**/B3LYP/6-311++G (3df, 3pd) level of theory (values are given in kcal/mol).

transition metals Mn and Fe prefer to form divalent molecules due to the stability of the d^5 and d^6 electronic configurations.[49]

Under UV light irradiation one hydrogen atom of the CH_3 group can be transferred further to the O atom in $CH_3Ti(O)H$ to form the $CH_2Ti(H)OH$ isomer. The $CH_2Ti(H)OH$ structure is 23.4 kcal/mol less stable than the ground-state $CH_3Ti(O)H$ isomer. The reaction on the singlet ground state was computed to proceed via a transition state (TS3) lying 51.4 kcal/mol above $CH_3Ti(O)H$ (Figure 7). A similar UV-induced α-H transfer has been observed for CH_3TiX to form CH_2TiHX (X = H, F) in reactions of Ti atoms with CH_4 and CH_3F. [20,46b]

Upon sample annealing, the $CH_2Ti(H)OH$ titano−vinyl alcohol absorptions decreased while the $(CH_3)_2Ti(H)OH$ titano−isopropyl alcohol absorptions increased. This implies that $CH_2Ti(H)OH$ activates a second methane with very low activation energy. As shown in Figure 7, the activation process is exothermic by about 32.1 kcal/mol. The reaction proceeds with initial formation of a $CH_2Ti(H)OH(CH_4)$ complex followed by a hydrogen-atom transfer via a transition state (TS4) lying 4.0 kcal/mol above the $CH_2Ti(H)OH + CH_4$ reactants. The energy barrier is quite low, and tunneling effects, which are common for hydrogen-atom transfer reactions, might be responsible for formation of $(CH_3)_2Ti(H)OH$ on annealing.[50] This reaction is analogous to that for CH_2TiH_2 and CH_4 to form the simple titano−propane $(CH_3)_2TiH_2$ molecule.[20]

The $CH_3Ti(O)H$ molecule reacted with CH_4 to form the $CH_3Ti(O)H(CH_4)$ complex on annealing. This complex was predicted to be bound by 10.9 kcal/mol with respect to $CH_3Ti(O)H$ and CH_4. The complex also rearranged to $(CH_3)_2Ti(H)OH$ under UV light irradiation. The $(CH_3)_2Ti(H)OH$ molecule is 2.2 kcal/mol less stable than the complex. The reaction from $CH_3Ti(O)H(CH_4)$ to $(CH_3)_2Ti(H)OH$ on the singlet ground state was computed to proceed via a transition state (TS5) lying 30.8 kcal/mol above the complex (Figure 7).

Laser evaporation of bulk TiO_2 target produces TiO as well as TiO_2. Theoretical calculations indicated that TiO_2 can also form a stable complex with CH_4 with a binding energy of 9.4 kcal/mol (see Supporting Information). However, no product due to the $TiO_2 + CH_4$ reaction was observed in the present experiments. Recent studies in our laboratory have shown that early transition-metal monoxides trapped in solid argon do not form stable complexes with argon; however, the dioxide molecules are coordinated by argon atoms with relatively strong metal−Ar binding energies.[51] Quantum chemical calculations indicated that TiO_2 could coordinate two argon atoms. The $TiO_2(Ar)_2$ complexes have a $^1A_1$ ground state with C_{2v} symmetry (see Supporting Information). The total Ti−Ar binding energy was predicted to be 10.9 kcal/mol, ca. 1.5 kcal/mol larger than that of the $TiO_2(CH_4)$ complex calculated at the same level of theory. Therefore, the TiO_2 absorptions observed in solid argon should be regarded as the $TiO_2(Ar)_2$ complex isolated in solid argon matrix; the $TiO_2(CH_4)$ complex cannot be formed via $TiO_2(Ar)_2 + CH_4$ reaction. In contrast, calculations on TiO(Ar) almost converged to separated TiO and Ar (Ti−Ar distance larger than 6 Å) with negligible binding energy, which indicated that TiO does not form a complex with Ar.

Conclusions

Methane activation by titanium monoxide molecules has been investigated using matrix isolation infrared spectroscopy and theoretical calculations. The titanium monoxide molecules prepared by laser evaporation of bulk TiO_2 target reacted with methane to form the $TiO(CH_4)$ complex. The complex rearranged to the $CH_3Ti(O)H$ titano−acetaldehyde molecule upon visible ($\lambda > 500$ nm) irradiation. The titano−acetaldehyde molecule sustained further photon-induced α-hydrogen transfer to give the $CH_2Ti(H)OH$ titano−vinyl alcohol molecule, which was characterized to be a simple carbene complex involving agostic bonding. A second methane activation occurred to form the $(CH_3)_2Ti(H)OH$ titano−isopropyl alcohol spontaneously on annealing. The $(CH_3)_2Ti(H)OH$ molecule also can be produced via UV photon-induced rearrangement of the $CH_3Ti(O)H(CH_4)$ complex. These molecules are identified by isotopic substitution and comparison to DFT frequency calculations. As shown in

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this study, the $TiO + CH_4$ reaction may serve as a model system in understanding the intrinsic mechanism of transition-metal-mediated alkane conversion.

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Supporting Information Available: Complete ref 36 and absolute energies, vibrational frequencies and intensities, and geometries (as Cartesian coordinates) of all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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