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Reactions of Laser Ablated Ti Atoms with Hydrogen during Condensation in Excess Argon. Infrared Spectra of the TiH, TiH_2, TiH_3, and TiH_4 Molecules

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Abstract: Reactions of pulsed-laser evaporated Ti atoms with H_2 in a condensing argon stream gave TiH, TiH_2, TiH_3, TiH_4, and polymeric species. The main difference between pulsed laser and thermal evaporation Ti atom reactions is the observation of all four products directly after sample deposition and the appearance of the new TiH and TiH_3 radicals with laser evaporation. The assignments were based on concentration dependence and isotopic substitution and were confirmed by SCF frequency calculations. The stable D_{3h} titanium trihydride radical was identified from agreement between calculated and observed values for the eight active stretching frequencies for TiH_3, TiH_2D, $TiHD_2$, and TiD_3. Both experimental and theoretical results show that H atoms play an important role in the reaction mechanism.

Introduction

Reactions of titanium atoms with small molecules are of chemical interest as such products may play a fundamental role in catalytic and chemisorption processes. However, little experimental data is available for titanium hydrides. The formation of TiH_4 was first reported from the mercury-photosensitized decomposition of a $TiCl_4$–H_2 mixture.[1] The only spectroscopic data for titanium hydrides are assignments to TiH_2 and TiH_4 in solid krypton (and argon).[2] This work codeposited Ti atoms from a filament at 1380–1460 °C with H_2/Kr (Ar) mixtures, and weak new product bands which grew markedly on $\lambda > 580$ nm photolysis were observed. Recently titanium hydride thin films have been grown by reactive cathode sputtering using H_2/Ar gas and by e-beam physical vapor deposition.[3] In addition, theoretical investigations have been devoted to quantum chemical calculations on TiH and TiH_4, and titane is calculated to be a tetrahedral molecule.[4–8]

Recent investigations with hydrogen and aluminum have shown that laser ablation can lead to more rich chemistry than ordinary evaporation and change considerably the relative yields of the initial products. For example in the Al + H_2 system thermal evaporation of Al atoms gave very little product formation but selective photolysis gave AlH_2 and broadband photolysis gave AlH_3.[9,10] On the contrary laser ablated Al atoms produced the AlH molecule as the primary product, and the amount of AlH_2 was much less than AlH. Broadband photolysis gave AlH_3, and the presence of AlH led to the formation of numerous dimers.[11]

Comparing these results with thermal studies on the Ti + H_2 system,[2] it was decided to reinvestigate Ti + H_2 using the laser ablation method. The TiH, TiH_2, TiH_3, and TiH_4 molecules were observed in the infrared spectrum immediately after deposition, which indicated a different mechanism of reaction to form novel titanium hydrides.

Experimental Section

The technique for pulsed laser evaporation of Ti is identical with that employed in recent Al studies.[11] Laser power was varied from 30 to 100 mJ/pulse at the titanium target (commercial, 99%, sheet). Concentrations of gas mixtures (H_2/Ar, HD/Ar, D_2/Ar, H_2/D_2/Ar) were 2–10%. Typical rates of deposition were 2–4 mmol/h onto a 10 ± 1 K CsI window for 2–4-h periods. FTIR spectra were recorded on a Nicolet 750 at 0.5 cm^{-1} resolution using a MCT detector. Annealing and photolysis with a 175-W mercury street lamp (Philips H39KB) with the globe removed were also done.

Results

Infrared spectra of Ti + H_2, Ti + D_2, Ti + HD, and Ti + H_2 + D_2 systems and SCF calculations on possible reaction products will be presented.

Ti + H_2 System. Typical spectra from the Ti + H_2/Ar system are shown in Figure 1 and the bands are listed in Table 1. Spectra can be divided into three groups depending on reagent concentration. With low concentration of hydrogen and low laser power only one weak 1435.5-cm^{-1} band was observed. Increasing laser power led to increase of this band and appearance of new absorptions at 1640.5/1632.0, 1554.2, 1518.6, 1506.6, 1496.9, 1485.2, 1464.2, and 1452.3/1444.7 cm^{-1}. After deposition the 1485.2-cm^{-1} band had almost the same intensity as the 1435.5-cm^{-1} band, and intensities of other bands were also almost the same. Annealing changed this distribution: the 1435.5-cm^{-1} band increased and became the strongest band in the spectrum. Among the bands in the 1500-cm^{-1} region, the most intense after annealing was the 1506.6-cm^{-1} band.

Deposition with higher laser power and higher hydrogen concentration gave different spectra, which are shown in Figure 1. The 1435.5-cm^{-1} band was very strong, and new absorptions appeared at 1385.3, 1580.6/1578.3, and 1663.8/1656.7 cm^{-1}. The former is labeled TiH_2 and the latter TiH_4 as assigned by the Rice group.[2] Bands near 1500 cm^{-1} were also observed and the strongest band among them was 1496.9 cm^{-1}. Slightly varying laser power led to alteration of intensity of the 1385.3-cm^{-1} band: decreasing power reduced this band to a shoulder on the 1389.1-

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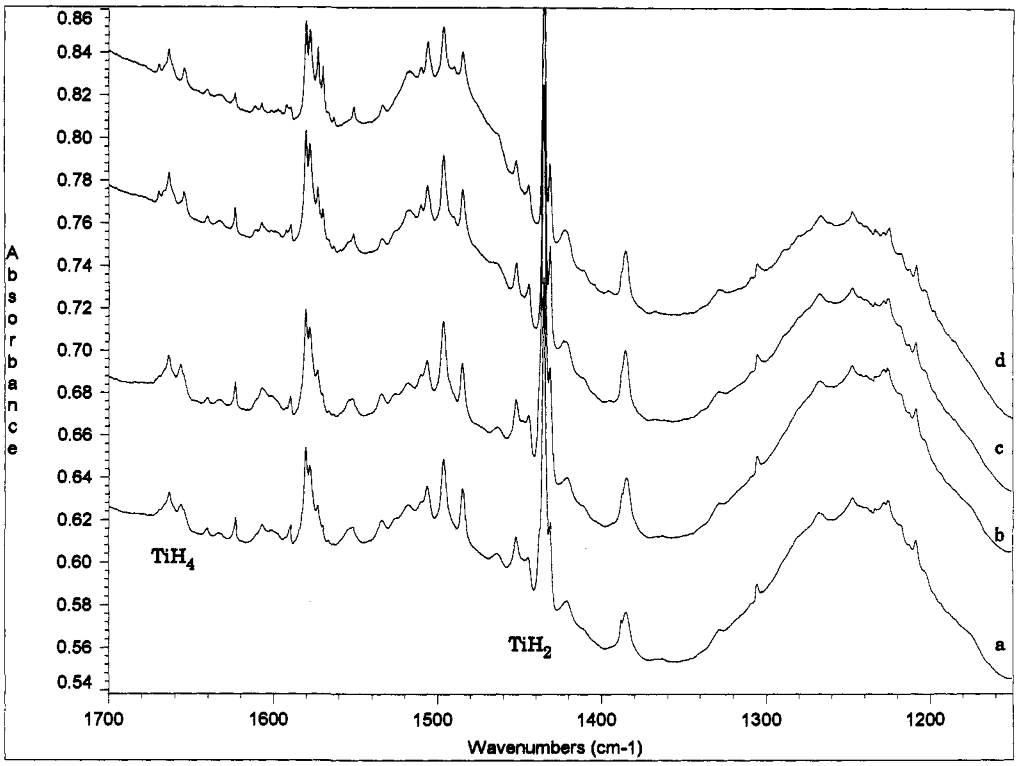

Figure 1. Infrared spectra in the 1700–1150-cm^{-1} region for pulsed-laser evaporated Ti atoms and 5% H_2 in argon: (a) sample deposited at 10 ± 1 K for 2 h, (b) after broadband photolysis for 40 min, (c) after annealing to 21 ± 1 K, and (d) after annealing to 30 ± 1 K.

Table 1. Infrared Absorptions (cm^{-1}) from the Reaction of Pulsed-Laser Evaporated Ti Atoms with H_2, D_2, and HD in Excess Argon

H_2	D_2	HD	assignment
1663.8	1205.6	1662.2, 1206.3	TiH_4
1656.7	1200.0	1655.3, 1209.7	
1640.5	1174.8	1641.1	Ti_xH_y
1632.0	1169.3	1634.7	
1580.6	1147.2	1640.7, 1182.0	TiH_3
		1602.1, 1156.0	
		1578.4, 1147.7	
1518.5	1089.1	1518.4, 1092.8	Ti_xH_y
1506.6	1086.1	1506.8, 1085.0	
1496.9	1081.0	1500.7, 1079.0	
1485.2	1070.9	1485.2, 1070.9	
1464.2			$TiH_2(H_2)_x$
1452.3	1052.9		
1447.7	1049.0		
1435.5	1041.0	1466.7, 1055.7	TiH_2
1422.7	1031.0		$(TiH)(H_2)$
1404.4	1031.0	1404.4, 1031.0	$(HO_2)(H_2)$
1389.1	1019.9	1389.1, 1019.9	HO_2, DO_2
1250	880	1250, 880	Ti_xH_y
1385.3	1003.6	1385.3, 1003.6	TiH
1104.7		1104.7	$(HO_2)(H_2)$
1100.7		1100.7	HO_2
987	987	987	TiO
917	917	917	TiO_2
904.5	644.2	904.5, 644.2	Ar_nH^+
500			Ti_xH_y

cm^{-1} band of HO_2,[12] and increasing power gave the 1389.1-cm^{-1} band as a shoulder of the 1385.3-cm^{-1} band. It is important to emphasize that appearance of the 1663.8/1654.6-, 1580.6/1578.3-, and 1385.3-cm^{-1} bands depended more strongly on laser power than on hydrogen concentration. No bands were observed for Ti reaction products with water[13] as water was present here only as a trace impurity.

Below 1000 cm^{-1} titanium oxides were observed at 987 cm^{-1} for TiO and 917 cm^{-1} for TiO_2.[14,15] In addition the 904.5-cm^{-1} absorption for Ar_nH^+ was detected[16] and a broad band near 500 cm^{-1} was also observed.

Photolysis of this system led to an increase in intensities of the 1385.3-, 1435.5-, 1580.6/1578.3-, and 1663.8/1654.6-cm^{-1} bands and a slight decrease in the intensity of the 1485.2-cm^{-1} band. Annealing into the 18–22 K range led to increasing mostly 1385.3- and 1435.5-cm^{-1} bands and broad bands at 1500, 1250 and 500 cm^{-1}. The bands at 1580.6/1578.3 and 1663.8/1554.6 cm^{-1} grew very slightly and the 1485.2-cm^{-1} band slightly decreased on annealing to 25–30 K.

Finally, the titanium target was pulse-laser ablated into condensing argon, and the only bands observed are due to titanium oxides.

Ti + D_2 System. Infrared spectra of this system are presented in Figure 2. The shape and intensity distribution were almost identical with those described above. Depending on Ti and D_2 concentration, it is also possible to again separate three cases. As in the first system, under the lowest concentration of hydrogen and laser power, a weak 1041.0-cm^{-1} band (labeled TiD_2) was observed. Increasing laser power led to the appearance of new bands in the 1050–1100-cm^{-1} region with behavior analogous to that for the bands in the 1500-cm^{-1} region for H_2. With higher laser power and hydrogen concentration three new bands at 1003.6, 1147.2/1144.4, and 1205.6/1200.0 cm^{-1} (labeled TiD_4) appeared in the spectra. On annealing to 25–30 K two broad bands at 1090 and 880 cm^{-1} increased in intensity.

Ti + HD System. Infrared spectra of this system are presented in Figure 3. As expected new bands are near corresponding bands from the H_2 and D_2 systems (Table 1), and these bands revealed the same behavior under varying conditions of deposition. One fact is very important: the bands at 1485.2, 1435.5, 1070.9, and

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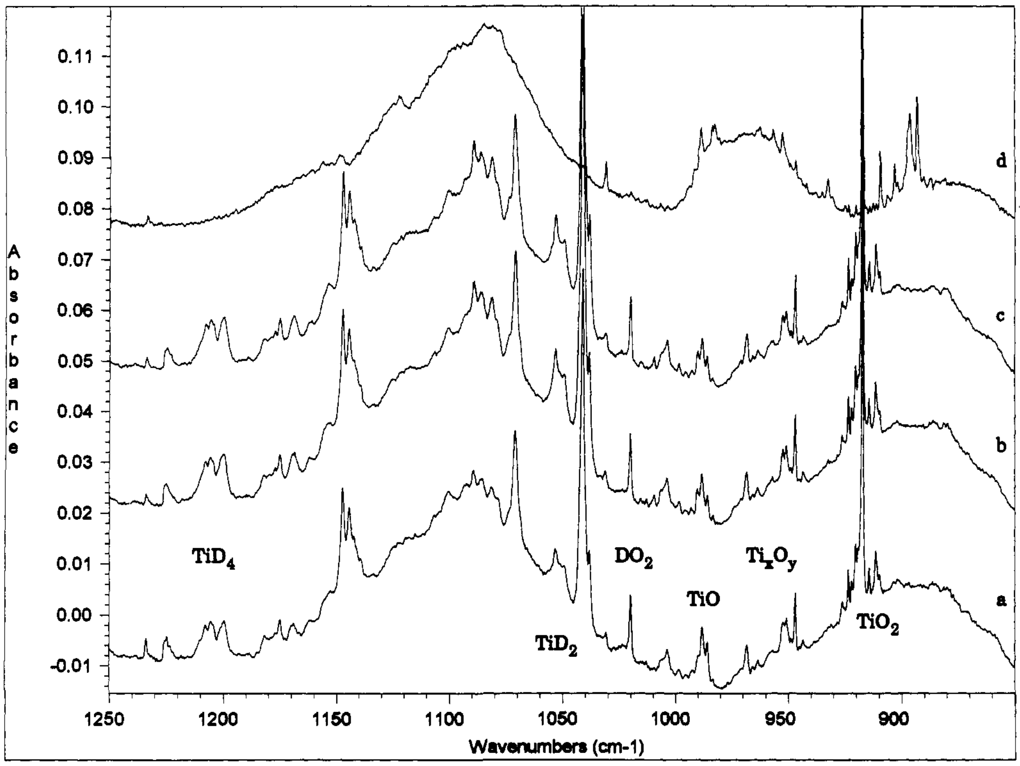

Figure 2. Infrared spectra in the 1250–850-cm^{-1} region for pulsed-laser evaporated Ti atoms and 5% D_2 in argon: (a) sample deposited at 10 ± 1 K for 2 h, (b) after broadband photolysis for 30 min, (c) after annealing to 14 ± 1 K, and (d) after annealing to 27 ± 1 K.

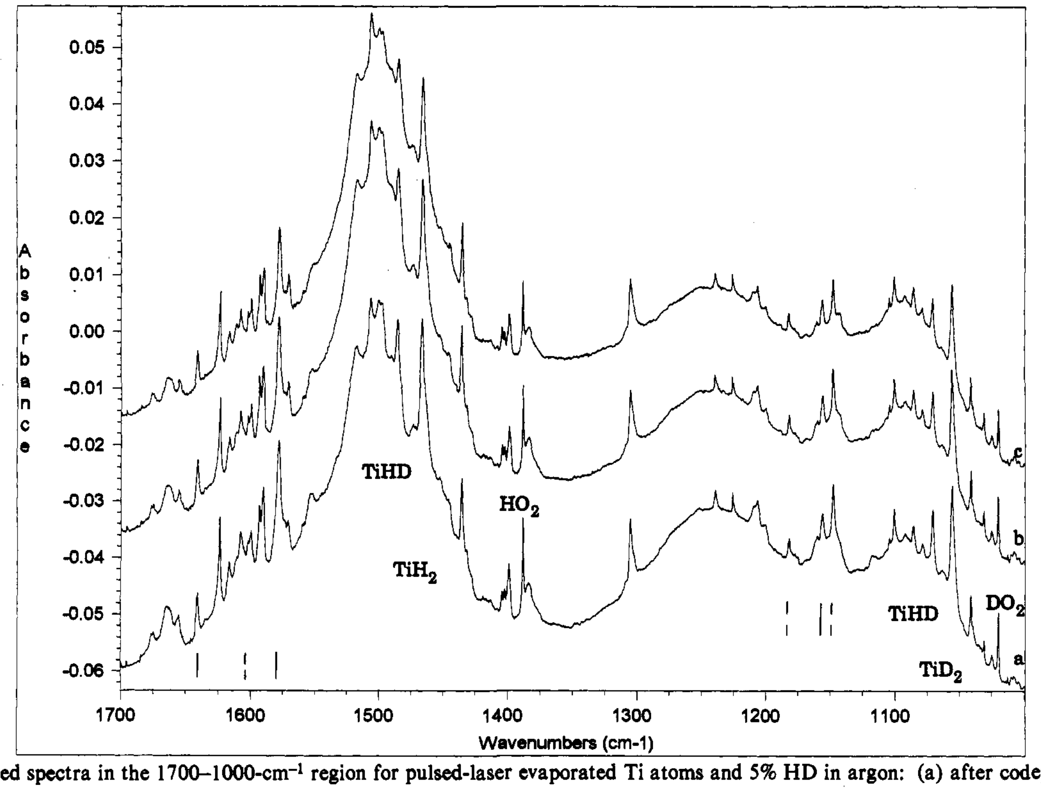

Figure 3. Infrared spectra in the 1700–1000-cm^{-1} region for pulsed-laser evaporated Ti atoms and 5% HD in argon: (a) after codeposition at 10 ± 1 K for 3 h, (b) after annealing to 14 ± K, and (c) after annealing to 20 ± 1 K.

1041.0 cm^{-1} were observed in these experiments, and the intensities of the 1485.2- and 1070.9-cm^{-1} bands were larger than intensities of the 1435.5- and 1041.0-cm^{-1} bands, respectively. Weak bands were also observed at 1385.2 and 1003.6 cm^{-1}.

Ti + H_2 + D_2 System. Spectra of the mixed system are presented in Figure 4 at low concentration. It is important to note that weak 1466.5- and 1055.7-cm^{-1} bands were observed in these experiments together with the 1435.5- and 1041.0-cm^{-1} bands. At higher concentration the 1666.7- and 1385.2-cm^{-1} bands from H_2 experiments and 1206.8- and 1003.6-cm^{-1} bands from D_2 experiments were stronger.

SCF Calculations. In addition to the known TiH_2 and TiH_4 molecules, the new molecules TiH and TiH_3 can also be formed. In order to determine reaction mechanisms, it is necessary to estimate the thermochemistry for this system. Also the knowledge about relative band positions and intensities can provide other

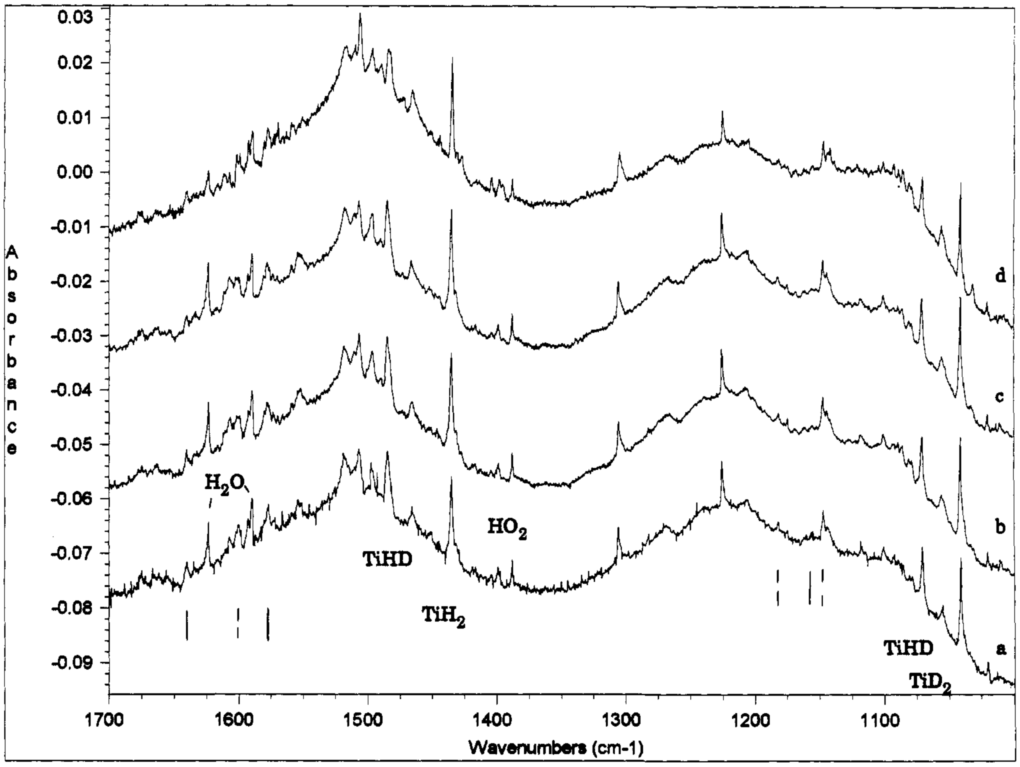

Figure 4. Infrared spectra in the 1700–1000-cm^{-1} region for pulsed-laser evaporated Ti atoms and 1% H_2, 1% D_2 in argon: (a) after codeposition at 10 ± 1 K for 2 h, (b) after broadband photolysis for 30 min, (c) after annealing to 14 ± 1 K, and (d) after annealing to 25 ± 1 K.

evidence for assignments. With this goal quantum chemical calculations for TiH_x molecules (x = 1–4) were performed.

All calculations were done at the SCF/UHF level using the ACES II program.[17] The Dunning's DZP basis set (built in the ACES II program) was used for hydrogen and Wachters[18] uncontracted GTO 14s9p5d or 14s11p6d basis sets for Ti. The last basis set was obtained from the first by adding two p-functions with the exponents 0.4 and 0.08 and one diffuse d-function with the exponent 0.072. These exponent values were obtained after minimization of Ti atom ground state (^3F) energy. The d-exponent value was the same as used earlier.[8]

Calculations with the simple 14s9p5d basis set did not produce results comparable with earlier calculations for the TiH and TiH_4 molecules;[6,8] hence only calculations with the 14s11p6d basis set will be presented. It is clear that the SCF method is not adequate for calculations of Ti containing compounds as correlation and relativistic effects are excluded in this case so these results should be considered as a first approximation. The important point is that SCF calculations produce a correct qualitative picture. Results of these calculations are presented in Tables 2–4 and are in good agreement with those obtained earlier for TiH and TiH_4.

For the TiH molecule a multiplicity 4 ground state was found. The big difference between the present and earlier calculated frequencies is the higher level of calculation used earlier.[5,6] For the TiH_2 molecule minima were found on singlet and triplet potential surfaces. The triplet molecule is much more stable that the singlet by 55 kcal/mol. It is interesting to note that for both molecules symmetric vibrations should not be observed because the triplet molecule is almost linear and the HTiH angle is the singlet molecule is 160°. For both molecules the calculated bending mode is much less than that reported in Kr matrices (496.1 cm^{-1})[2] which raises doubt about this assignment. For the TiH_3 molecule only one doublet minimum corresponding to the D_{3h} structure was found after starting with C_{3v} and C_1 structures.

Table 2. Ab Initio Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for the TiH and TiH_2 Molecules

TiH	1471 (239)[a]	1407[b]
TiD	1051 (122)[a]	
E(SCF) (au)	–848.93536	
R (Å)	1.849	1.83
	TiH_2	
	singlet	triplet
TiH_2	1658 (27) A_1	1503 (2) A_1
	1525 (604) B_1	1475 (627) B_1
	312 (424) A_1	56 (679) A_1
TiHD	1597 (270)	1489 (309)
	1131 (210)	1064 (170)
	272 (323)	49 (520)
TiD_2	1173 (14) A_1	1064 (1) A_1
	1100 (314) B_1	1064 (327) B_1
	225 (221) A_1	41 (354) A_1
E(SCF) (au)	–849.43280	–849.51983
R (Å)	1.818	1.872
HTiH (deg)	160	174 "probably linear"

[a] Intensities in parentheses (km/mol). [b] CASSCF/CI(SD), ref 6.

Table 3. Ab Initio Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for the TiH_3 (D_{3h}) Molecule[a]

TiH_3	TiH_2D	$TiHD_2$	TiD_3
1747 (0) A_1'	1716 (289) A_1	1681 (5971) A_1	1236 (0) A_1'
1646 (1007) E'	1644 (985) B_1	1216 (231) A_1	1184 (534) E'
576 (138) E'	1202 (429) A_1	1187 (560) B_1	412 (69) E'
336 (789) A_2''	573 (129) A_1	525 (107) B_1	245 (418) A_2''
	474 (95) B_1	413 (72) A_1	
	309 (666) B_2	279 (542) B_2	

[a] R = 1.758 Å, E(SCF) = –850.06594 au, intensities in parentheses.

The TiH_4 molecule has T_d symmetry which is in agreement with previous calculations.[8] The differences in SCF energy and frequencies probably arises from different basis sets for hydrogen used in the present and previous works.[8] Isotopic frequencies are compared in Table 4 for TiH_4, TiD_4, TiH_3D, and $TiHD_3$ for different calculations. The present calculated frequencies for

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Table 4. Ab Initio Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for the $TiH_4(T_d)$ Molecule

TiH_4		TiH_3D		TiD_4		$TiHD_3$		TiH_2D_2	
A_1	1957 (0),[a] 1937,[b] 1828[c]	A_1	1924 (212), 1905, 1810	A_1	1384 (0), 1370, 1293	A_1	*1850* (694), 1833, 1772	A_1	1889 (440), 1871, 1791
T_2	*1811* (1058), 1795, 1752	E	*1810* (1043), 1794, 1752	T_2	*1302* (565), 1291, 1259	A_1	1359 (212), 1345, 1283	B_1	*1809* (1029), 1793, 1752
E	637 (0), 634, 587	A_1	1323 (511), 1311, 1268	E	450 (0), 449, 415	E	*1304* (582), 1293, 1260	A_1	1339 (374), 1326, 1275
T_2	547 (167), 548, 467	E	612 (28), 611, 560	T_2	392 (86), 396, 338	E	534 (43), 534, 485	B_2	*1306* (600), 1294, 1260
		A_1	539 (158), 545, 466			E	415 (69), 418, 364		
		E	471 (111), 475, 409			A_1	393 (89), 397, 339		

[a] E(SCF) = −850.58771 au, R = 1.682 Å, intensities (km/mol). [b] E(SCF) = −850.60316 au, R = 1.697 Å, ref 8. [c] E(CCSD) = −850.78055 au, R = 1.710 Å, ref 8.

TiH_2D_2 stand in the same relationship to those of the earlier study,[8] and only the stretching modes are included for comparison.

The main result of these calculations is increasing valence Ti–H stretching frequencies in the TiH–TiH_2–TiH_3–TiH_4 series. On the basis of these calculations and the experimental observations it is possible to identify the product molecules.

Discussion

From the above experimental observations, it is clear that the reaction between hydrogen and titanium is rather complicated. One normally expects the appearance of products to depend strongly on concentration but the unusual observation is strong dependence of spectra on laser power. It indicates that processes with high-energy atoms or ultraviolet photolysis which always accompanied laser ablation may play a considerable role in activation of the reactions. Assignment of spectral bands will be presented.

TiH. The lowest frequency product band at 1385.3 cm^{-1} is assigned to the TiH molecule which is in good agreement with calculations (Table 2). This band produced only one isotopic counterpart in HD and $H_2 + D_2$ systems as required for a product with one hydrogen atom. The isotopic ratio 1.3803 is slightly lower than the harmonic value (1.39990 due to cubic anharmonicity in the Ti–H vibrational potential function. We expect the gas-phase fundamental to be found at 1405 ± 10 cm^{-1}. The intensity of the 1385.3-cm^{-1} band depended strongly on laser power and on hydrogen concentration as both were required to sustain the "glow discharge" condition in the plume extending from the Ti target to the cold window where H atoms are formed. These H atoms can react with Ti atoms to produce TiH.

TiH_2. The bands at 1435.5 and 1041.0 cm^{-1} in Ti + H_2 and Ti + D_2 systems and 1466.5 and 1055.7 cm^{-1} in Ti + HD and Ti + H_2 + D_2 systems were assigned to TiH_2, TiD_2, and TiHD molecules in the earlier work.[2] The H/D ratio (1.3790) is only slightly lower than the value observed for TiH/TiD. The TiH_2 molecule should be the first reaction product; the behavior of the 1435.5-cm^{-1} band is in agreement with this proposition as it was seen under the lowest laser power and hydrogen concentration conditions. The present TiH_2 observations and assignment of the above bands are in agreement with those of the Rice group.[2] Ground state TiH_2 is probably the triplet molecule, although calculations with electron correlation are needed. The analogous TiF_2 molecule also has a nonlinear triplet ground state.[19,20]

The second band assigned earlier to the symmetric stretching mode (1070.9 cm^{-1}) was observed here to vary in relative intensity between 1 to 1 and 1 to 3 with the 1041.0-cm^{-1} antisymmetric TiD_2 stretching fundamental in solid argon whereas the Rice group[2] found a 1 to 10 relative intensity for these bands. The ν_1 mode of TiH_2 was assigned as 1483.2 cm^{-1} in solid argon by the Rice group.[2] The present 1485.2-cm^{-1} band is probably the same absorption; likewise this band varied from 1 to 1 and 1 to 10 with the 1435.5-cm^{-1} ν_3 fundamental and the Rice group reported a 1 to 16 relative intensity for the solid argon bands. The above lack of correlation in relative intensities suggests that the earlier ν_1 assignments to TiH_2 and TiD_2 are not correct; these modes are probably too weak to be observed in the infrared spectrum as predicted by the present calculations. Furthermore, it is impossible to connect any bands from the 500-cm^{-1} region with the bending mode of this molecule; the ν_3 assignment to triplet TiH_2 is in good agreement with SCF calculations, but the calculated isotopic spectra are not adequate as the A_1 mode in TiHD and B_1 and A_1 modes in TiD_2 are almost the same for the triplet species whereas the observed spectra revealed TiHD at 1055.7 cm^{-1} and TiD_2 at 1041.0 cm^{-1}. The singlet calculation is much worse in the upper region as TiHD is predicted to be 72 cm^{-1} higher than TiH_2 whereas TiHD was observed at 1466.7 cm^{-1}, only 31.2 cm^{-1} higher.

TiH_3. The bands at 1580.6 cm^{-1} and 1147.2 cm^{-1} are assigned to the TiH_3 and TiD_3 molecules. The H/D ratio (1.3778) is almost the same as that observed for the above hydrides. According to calculations (Table 3) three vibrations for TiH_2D and for $TiHD_2$ should be observed in the Ti–H and in the Ti–D stretching regions. In HD experiments new 1640.7-, 1602.1-, 1578.4-, 1182.0-, 1156.0-, and 1147.7-cm^{-1} bands were observed. The first, third, and fifth bands are assigned to A_1, B_1, and A_1 stretching modes of TiH_2D and the second, fourth, and sixth bands to A_1, A_1, and B_1 modes in $TiHD_2$, respectively, which are noted by vertical solid and broken lines in Figures 3 and 4. Note that the sharp 1580.6-cm^{-1} TiH_3 and 1147.2-cm^{-1} TiD_3 bands were not observed in the HD experiments. The six new mixed isotopic bands are in excellent agreement with the prediction of SCF frequency and intensity calculations. First the observed/calculated ratio (scale factor) for TiH_3 is 0.960 and that for TiD_3 is 0.969, which is appropriate agreement allowing for the differences in cubic anharmonicity for the observed Ti–H and Ti–D vibrations as compared to harmonic calculations.[21] Scale factors range from 0.953 to 0.972 for the six mixed isotopic bands, which confirms the identification of TiH_3 and the vibrational assignments.

The analogous TiF_3 molecule has been characterized as a trigonal planar species.[20]

TiH_4. The doublets at 1663.8/1656.7 and 1205.6/1200.0 cm^{-1} are assigned to the ν_3 (T_2) vibrations of TiH_4 and TiD_4, which is in an agreement with previous experimental work[2] and previous[8] and present calculations (Table 4). The observed/calculated ratios are 0.919 for TiH_4 and 0.926 for TiD_4, respectively, which are in good agreement considering anharmonicity.[19] According to frequency and intensity calculations, and taking into account the small yield of this molecule, two bands for each TiH_3D, TiH_2D_2, and $TiHD_3$ should be observed in the Ti–H and Ti–D regions. The E mode of TiH_3D and the B_1 mode of TiH_2D_2 are more intense than the A_1 mode of $TiHD_3$ in the Ti–H region, and the B_2 and E modes of TiH_2D_2 and $TiHD_3$, respectively, are more intense than the A_1 mode of TiH_3D in the Ti–D region. This leads to the observation of only two distinct bands in each region. The shifts between them are very small and close to the corresponding T_2 vibrations in TiH_4 and TiD_4. That is why in HD and H_2 + D_2 experiments only one band was observed in each region; however, new shoulders were observed on the red side of the TiH_4 band and on the blue side of the TiD_4 band as

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Table 5. Heats of Reactions Calculated from SCF Energies[a]

reaction	ΔE (kcal/mol)
$Ti + H_2 \rightarrow TiH_2$	2.5
$Ti + H_2 \rightarrow TiH + H$	57
$TiH + H_2 \rightarrow TiH_3$	0.4
$TiH_2 + H_2 \rightarrow TiH_4$	40
$TiH_2 + H_2 \rightarrow TiH_3 + H$	55
$TiH_3 + H_2 \rightarrow TiH_4 + H$	70
$Ti + H \rightarrow TiH$	−28
$TiH + H \rightarrow TiH_2$	−54
$TiH_2 + H \rightarrow TiH_3$	−30
$TiH_3 + H \rightarrow TiH_4$	−15

[a] The following SCF energies (au) were used: $E(H_2) = -1.13124$, $E(H) = -0.49764$, $E(Ti, {}^3F) = -848.39265$.

predicted by SCF frequency calculations. The T_2 deformation mode of titane should occur in the 500–400-cm^{-1} region. Due to overlapping and broadening it was impossible to resolve it from the broad 500-cm^{-1} band.

Polymeric and Complex Species. Bands in the 1500-, 1250-, and 500-cm^{-1} region are assigned to polymeric species Ti_xH_y based on their dependence on concentration and temperature. It is impossible now to suggest a more detailed assignment. Calculations on different TiH and TiH_2 dimers were not successful. However, the appearance of bands in two stretching regions indicates that these polymers should have terminal and bridged Ti–H bonds. The dimer species $HTi(H)_2TiH$ is a possibility. The broad 1500 cm^{-1} band decreased with decreasing H_2 concentration, but the broad 1250 cm^{-1} band remained at the lowest H_2 concentration. The latter could be due to a bridged $(TiH_2)_x$ species.

The 1485.2- and 1070.9-cm^{-1} bands have been ruled out as ν_1 modes for TiH_2 and TiD_2. These sharp bands appear in HD experiments with intensities comparable to those of the ν_3 modes of TiH_2 and TiD_2, which indicates a species involving a single H or at most two uncoupled H atoms. The HTiTiH dimer is suggested. Note that the strongest HAlAlH band was 55 cm^{-1} higher than the AlH fundamental.[11]

The bands at 1452.3/1444.7 and 1422.7 cm^{-1} were seen in spectra only when a high concentration of hydrogen was used and the 1435.5-cm^{-1} band was strong. These bands revealed almost the same isotopic ratios (1.3793 and 1.3799) as TiH_2 (1.3790) and are best identified as $TiH_2(H_2)_x$ complexes.

Reaction Mechanisms

Table 5 contains possible reactions leading to the formation of TiH_x molecules and the heats of these reactions. Two basic paths are important: reactions with H_2 and with H. Note that the reactions of Ti atoms and TiH molecules with H_2 have small positive heats of reaction. Even using the SCF energy for TiH_4 from previous work does not change the heat from positive to negative. Considering the reaction of Ti with H_2, the Rice group concluded that formation of the TiH_2 molecule may have a small negative value of heat.[2] Certainly the growth of this molecule on annealing suggests a spontaneous reaction, although another mechanism, namely the reaction of TiH and H, must be considered. In Ti + HD and Ti + H_2 + D_2 experiments, TiH_2, TiHD, and TiD_2 were observed. In the HD system the bands of TiH_2 and TiD_2 were weaker than those for TiHD. The reverse situation was found in H_2 + D_2 experiments. All of these observations confirm the involvement of H atom reactions and in particular the TiH + H reaction, which is calculated to be exothermic by 54 kcal/mol.

The data in Table 5 show that successive reactions with H atoms are involved in formation of the higher hydrides. The question is how many H atoms are present in the sample? It is necessary to emphasize one more time that TiH, TiH_2, TiH_3, and TiH_4 molecules were observed in spectra together with the HO_2 radical. The observation of HO_2 confirms H-atom participation in the matrix reactions.

Another possibility for formation of hydrides is reactions between electronically excited Ti(^{5}G) atoms and H_2 molecules or H atoms. Unfortunately we cannot estimate the amount of excited Ti atoms in our experiments.

The mechanism must involve reactions in the gas phase or the matrix surface during deposition. Two processes can lead to H-atom formation—far-UV photolysis from the plasma and collisions between very high kinetic energy Ti atoms and H_2 molecules. Similar pulsed laser experiments with Al in the gas phase have measured average kinetic energies in the 5-eV range[22] and matrix reactions of pulsed laser evaporated Al atoms with O_2 have given the OAlO insertion product, which requires activation energy.[23] The Ti atoms produced here clearly have excess kinetic energy. The present deposition conditions define a "glow discharge" in the region between the target and cold window and the dissociation of H_2 into atoms is probably occurring in this region. This explains the marked increase in yield observed as increasing laser power leads to increasing the energetic Ti atom concentration. The increasing of H_2 concentration also leads to increasing of both photolysis and collision efficiency. The activation energy required for the Ti + H_2 reaction can certainly be provided by hyperthermal Ti atoms from laser ablation.

Two further points must be made in comparison with the thermal Ti reactions. Figure 3b of that work clearly shows the presence of weak TiH_4 and TiH_2 bands after codeposition of H_2/Kr through the furnace with Ti atoms from a 1450 °C filament.[2] Either filament photolysis or reaction of Ti atoms on the high energy tail of the thermal distribution is occurring. The major TiH_2 and TiH_4 yield followed $\lambda > 580$ nm photolysis in that work. Photochemical activity was also found in the present experiments.

Conclusions

Pulsed laser evaporated Ti atoms react with H_2 molecules and H atoms to produce the TiH, TiH_2, TiH_3, and TiH_4 molecules. The main difference from thermal evaporation reactions is observation of all four molecules directly after sample deposition and the appearance of two new molecules, TiH and TiH_3. The latter D_{3h} radical species is identified from the eight infrared active stretching modes in the TiH_3, TiH_2D, $TiHD_2$, and TiD_3 molecules and the excellent agreement with SCF frequency calculations. The large yield of TiH_3 in these experiments underscores the stability of the titanium(III) hydride species. On the basis of experimental results and quantum chemical calculations it is concluded that reactions with H atoms play an important role in the reaction mechanism in the pulsed laser experiments. The thermal experiments involved only photochemical reactions of Ti with H_2, and as such gave only TiH_2 and TiH_4 as products. Thus the pulsed laser source of hyperthermal Ti atoms activated Ti for reaction and dissociated H_2 into atoms for further stepwise reactions.

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