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# Intracluster Ion−Molecule Reactions of $Ti^+$ with Methanol Clusters

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The intracluster ion−molecule reactions occurring within the titanium/methanol heterocluster ions are studied using a simple cluster source based on the mixing of the laser-ablated plasma with the supersonic expansion of a methanol vapor seeded in Ar carrier gas. The product ions are detected using a reflectron time-of-flight mass spectrometer. The mass spectra exhibit a major sequence of cluster ions with the formula $Ti^+(CH_3O)_2(CH_3OH)_n$, which are attributed to the hydrogen elimination reactions (−2H or $-H_2$) of $Ti^+$ ion within the heteroclusters. In addition, heterocluster ions of the types $Ti^+(CH_3O)(CH_3OH)_n$ and $Ti^+(CH_3O)_3(CH_3OH)_n$ also emerge throughout the observed mass spectra, indicating that consecutive H-eliminations by the $Ti^+$ ion occur for up to three methanol molecules. The results from isotope-labeling experiments suggest that H-elimination is the reaction path for O−H bond breaking in $Ti^+$−methanol heteroclusters. The observed $TiOH^+$ and $TiO^+$ ions are interpreted as arising from the insertion of $Ti^+$ ions into the C−O bond in $CH_3OH$, followed by $CH_3$- and $CH_4$-elimination, respectively, from the $[HO-Ti^+-CH_3]$ intermediate. The experiments also show that the chemical reactivity of heterocluster ions is greatly influenced by cluster size and argon stagnation pressure. The reaction energetics and formation mechanisms of the observed heterocluster ions are also discussed.

## I. Introduction

Numerous studies on the chemical reactions of transition metal ions with various molecules in the gas phase have been carried out to clarify the catalytic activity of metal ions as well as the mechanisms and intermediates in many important organometallic reactions.[1−7] The study of the gas-phase chemistry of these ions can provide information about their intrinsic chemical and physical properties and can contribute to a better understanding of their behavior in the condensed phase. For instance, the reactions of $Ti^+$ with small alkane molecules have been studied using a flow tube technique. The most intriguing finding of those studies is that $Ti^+$ is very active in the breaking of C−H bonds, leading to the dehydrogenation of the alkanes.[8−11] The alkanes were observed to be cleaved by the metal ion in an oxidative−addition reaction, which was explained by either a C−H or C−C insertion mechanism.

Gas-phase bimolecular reactions of $Ti^+$ with water at thermal energies have been studied by Castleman and co-workers using a selected ion drift tube technique coupled with a laser vaporization source.[12] They attributed the presence of the primary product ion $TiO^+$ to $Ti^+$ insertion into the O−H bond, forming an $H-Ti^+-OH$ intermediate. The dehydrogenation channel proceeds from the intermediate by hydrogen migration to form $H_2-Ti^+-O$, which then loses $H_2$ to produce $TiO^+$.[13] Armentrout and co-workers have also studied the reaction of $Ti^+$ with $H_2O$ using a guided ion beam tandem mass spectrometer.[14] They, however, suggested that $H_2$ elimination from the $H-Ti^+-OH$ species occurs through a four-centered transition state.

The substitution of one H atom in $H_2O$ by the more bulky $CH_3$ group is expected to alter reaction pathways, because there are three different chemical bonds (C−H, C−O, and O−H) in the $CH_3OH$ molecule. The $Ti^+ + CH_3OH$ system has been the subject of previous investigations. Castleman and co-workers reported insertion reactions of $Ti^+$ ions into the C−H, C−O, and O−H bonds of methanol, producing $TiO^+$, $TiOH^+$, $Ti(CH_2O)^+$, and $Ti(CH_3O)^+$ as the primary reaction products.[12] Detailed knowledge of which bonds in the $CH_3OH$ molecules are activated by the $Ti^+$ ion is a primary motivation for much of the present work.

Although there have been numerous investigations of the reaction products formed in gas-phase ion−molecule reactions, there are few reported cases of chemical reactions taking place within the heterocluster ion itself. The study of the product distribution of metal ion−solvent heteroclusters provides valuable information on the variation of reaction pathways with increasing cluster size, reflecting the transition from gas-phase reactions to solution-phase reactions. Ion−molecule reactions of $Ti^+$ with methanol clusters have been studied by Sato and co-workers using a laser ablation-molecular beam method.[15] They suggested that the elimination of a hydrogen molecule (reaction 1) from the clustered complex ions $Ti^+(CH_3OH)_n$ is the dominant process producing the fragment ions $Ti^+(CH_3OH)_{n-1}CH_2O$:

$$Ti^+(CH_3OH)_m \rightarrow Ti^+(CH_3OH)_{n-1}CH_2O + H_2 + (m-n)CH_3OH \quad (1)$$

In a recent study of the reactions of laser-generated $Ti^+$ with methanol clusters, El-Shall and co-workers reported that the major $Ti^+$-containing ions correspond to the sequence $TiO^+(CH_3OCH_3)(CH_3OH)_n$, which they attributed to the catalytic conversion of methanol dimer into dimethyl ether by $TiO^+$ (reaction 2).[16]

$$Ti^+(CH_3OH)_m \rightarrow TiO^+(CH_3OH)_{m-1} + CH_4 \rightarrow TiO^+(CH_3OCH_3)(CH_3OH)_n + H_2O \quad (2)$$

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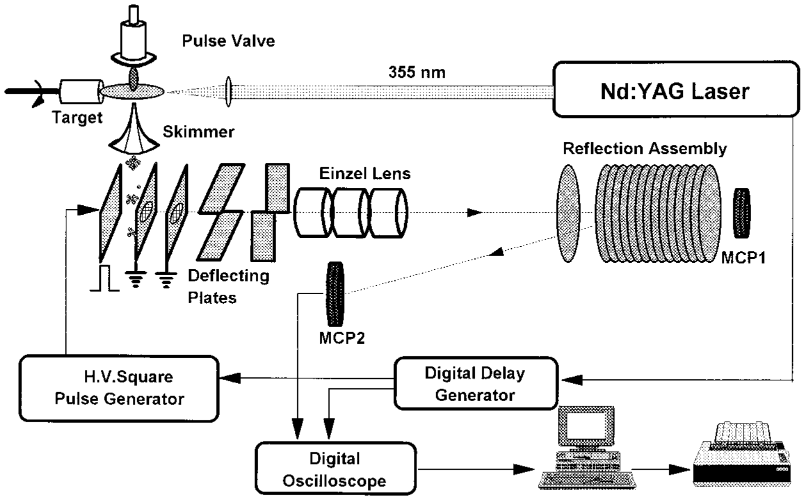


**Figure 1.** Schematic diagram of the experimental setup for the laser ablation-molecular beam source coupled with a reflectron time-of-flight mass spectrometer.

The above studies raise the interesting question as to whether $Ti^+$ ion is primarily oxidized to form $TiO^+$ (reaction 2) or primarily inserted into the methanol molecule followed by H-eliminations within the heteroclusters (reaction 1). The reliable identification of these reaction products is important for understanding the catalytic reaction mechanism. Despite the significance of these reactions and the effort that has been put into their study, general agreement as to the reaction pathways of even the simplest reactions has not been reached. The study of the specific chemical dynamics of reaction within a cluster ion is especially interesting because it is possible to directly observe how chemical reactivity changes as a function of stepwise solvation, simply by monitoring the changes in reaction channel versus the cluster size.[17-20]

The general objective of the present work is to investigate the reactivity of $Ti^+$ with respect to the breaking of the C−H, C−O, and O−H bonds in methanol molecules within the heterocluster ions. To probe the cluster reactivity, we examined the reactions using a combination of laser ablation and supersonic gas expansion. In this study, partially deuterated methanol is used to elucidate the reaction mechanisms for methanol activation by $Ti^+$. Studies of the reactivity of titanium−methanol heteroclusters as a function of Ar stagnation pressure and cluster size also aid the understanding of the influence of solvation and the nature of the H-elimination reactions of the $Ti^+$ ion on a molecular level.

## II. Experimental Section

A schematic diagram of the laser ablation-molecular beam (LA-MB)/reflectron time-of-flight mass spectrometer (RTOFMS) is given in Figure 1. It consists of two differentially pumped chambers: the source and the detection regions. Reactant $(CH_3OH)_n$ clusters are introduced through a pulsed nozzle (General Valve; 0.8 mm orifice diameter) in the source chamber, which is pumped by a 2000 L $s^{-1}$ diffusion pump fitted with a water-cooled baffle. Argon carrier gas is bubbled through a reservoir containing the liquid methanol at room temperature. After opening the valve, the third harmonic output (355 nm) of a Q-switched Nd:YAG laser (10 ns pulse width) strikes the rotating solid Ti target located 2 cm downstream from the nozzle. The laser beam was focused by a 35 cm focal length lens to a spot size of $\leq 1$ mm$^2$. The laser fluence at the target surface was varied in the range 10−100 mJ/cm$^2$. There is no cooling of the $Ti^+$ ions until they encounter the Ar/methanol beam. This means there are many metastable excited-state $Ti^{+*}$ in the metal reactant beam. The laser-ablated metal ions perpendicularly cross the expansion stream 1 cm from the target, where they react with the methanol clusters. The clusters are skimmed by a 1 mm conical skimmer and cooled collisionally as they travel down the detection region, which is pumped by a 300 L $s^{-1}$ turbomolecular pump. The nozzle−skimmer distance is 4 cm. The resulting pulsed beam with pulse duration of about 200 $\mu$s enters the extraction region of a RTOFMS, placed 10 cm downstream from the nozzle. Under usual operating conditions, the pressures in the source and detection chambers are always below $3 \times 10^{-5}$ and $5 \times 10^{-7}$ Torr, respectively.

We study the positive ions that are produced directly from the plasma/reactant gas mixing without the use of postionization. Following a delay of typically 50−200 $\mu$s after the laser shot, the positive ions are extracted by a +2200 V pulsed electric field, applied to the repeller. The ion extraction pulse (Directed Energy, Inc., GRX-3.0K-H) has a rise time of 40 ns and duration of 1 $\mu$s. The delay times between the valve opening, the laser firing, and ion extraction pulse are adjusted to obtain the maximum signal intensities of heteroclusters. The accelerated ions then travel through a 1 m long field-free region, which terminates at a double stage reflectron (R. M. Jordan Co.) located at the end of the flight tube. From the reflectron, the ions travel an additional 64 cm back to a 40 mm microchannel plate (MCP) detector. The mass spectrum is recorded by a 500 MHz digital oscilloscope (LeCroy 9350A) coupled with a personal computer. For acceptable signal-to-noise ratios, all mass spectra in the present experiment were obtained by a cumulative collection of 1000 laser shots at a repetition rate of 10 Hz. Spectrophotometric grade $CH_3OH$ (99.9%) and $CH_3OD$ (>99.5% D) (Aldrich Chemical) were used after further purification in a series of freeze−pump−thaw cycles to remove dissolved atmospheric gases and other impurities of high vapor pressure.

## III. Results

A typical TOF mass spectrum of the products of reaction between $Ti^+$ and methanol clusters is displayed in Figure 2. The spectrum was obtained using a laser pulse energy of 15 mJ/cm$^2$ and an argon stagnation pressure of 1 atm. We observe a pentad of peaks corresponding to the Ti isotopes ($^{46}Ti$, 8.0%; $^{47}Ti$, 7.3%; $^{48}Ti$, 73.8%; $^{49}Ti$, 5.5%; $^{50}Ti$, 5.4%);[21] the intensities of these isotopomers reflect their natural abundance. In the low

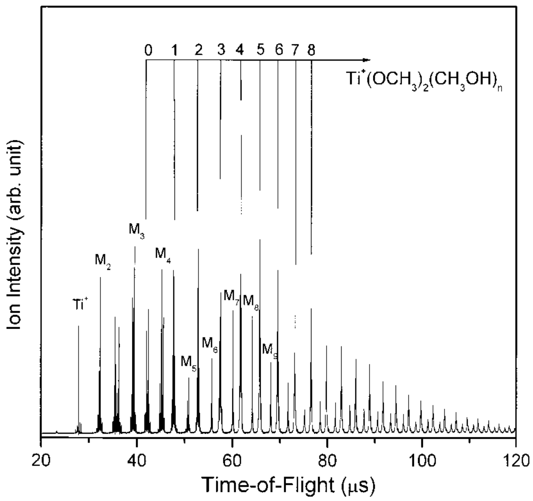


**Figure 2.** Time-of-flight mass spectrum of the cluster ions produced from the reactive collisions of laser-ablated $Ti^+$ and methanol clusters seeded in 1 atm Ar. $M_n$ denotes $(CH_3OH)_nH^+$ ions. The laser fluence is 15 mJ/cm$^2$.

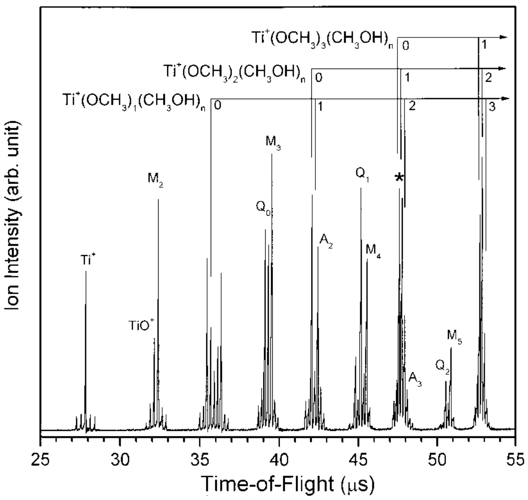


**Figure 3.** Time-of-flight mass spectrum showing the product ions in the low-mass region from the reactions of $Ti^+$ with $(CH_3OH)_n$: $A_n$, $Ti^+(CH_3OH)_n$; $M_n$, $(CH_3OH)_nH^+$; $Q_n$, $TiO^+(OCH_3)(CH_3OH)_n$. The peak labeled as * is for $Ti^+(OCH_3)_3$.

mass region, the mass spectrum exhibits a major sequence of $(CH_3OH)_nH^+$ cluster ions (labeled as $M_n$), which can be attributed to protonated clusters formed by the protonation of the generated parent cluster ions. Similar results have also been reported in electron impact[22,23] and multiphoton[24] ionization mass spectrometry. These species presumably derive from electron impact ionization by the free electrons escaping from the expanding plasma of laser ablation.

The characteristic abundance of Ti isotopomers, as observed in the mass peak of the $Ti^+$ ion, enables its complexes with methanol clusters to be readily identified. Hereafter, the Ti we refer to is the most abundant $^{48}Ti$ isotope. The prominent peaks in the high-mass region consist of $Ti^+(OCH_3)_2(CH_3OH)_n$ heterocluster ions with the characteristic size distribution. Though these peaks appear to fit the formula $Ti^+(CH_3OH)_n$, careful mass analysis of the spectrum reveals that these peaks in fact correspond to $Ti^+(OCH_3)_2(CH_3OH)_n$ ions, formed from the hydrogen elimination reaction ($-H_2$ or $-2H$) of $Ti^+(CH_3OH)_n$ ions. These methoxy-rich fragment ions are observed with up to 30 methanol units in the present experiments. This result implies that the $Ti^+$ ion reacts with $CH_3OH$ molecules solvated within the heteroclusters. The intact cluster ions $Ti^+(CH_3OH)_n$ stem from the association reaction between $Ti^+$ and methanol clusters, possibly followed by evaporation of methanol molecules.

$$Ti^+ + (CH_3OH)_m \rightarrow [Ti^+(CH_3OH)_m]^* \rightarrow Ti^+(CH_3OH)_n + (m - n)CH_3OH \quad (3)$$

The methanol evaporation results from the excess kinetic energy of the laser-ablated $Ti^+$ ions and also from the exothermicity of the ion−molecule association reactions. Titanium has a lower ionization potential than methanol. IP values are 6.82 and 10.85 eV for Ti and $CH_3OH$, respectively. Hence, the positive charge in the heterocluster is expected to reside on Ti, once the complex is formed in the source. Evidence for this claim has been provided by several beam experiments on the formation of the metal ion−organic molecule or −rare gas clusters.[25,26]

One of the interesting features of the mass spectrum of the heteroclusters is that the intensities of the $Ti^+(OCH_3)_2(CH_3OH)_n$ ion exhibit a local maximum at $n = 4$. This finding is constant over a wide range of stagnation pressure and is also independent of the laser fluence (i.e. it is independent of the cluster distribution produced by the reactive collisions), indicating that the $Ti^+(OCH_3)_2(CH_3OH)_4$ ion has a particularly stable geometry. Detailed structural information is not yet available for the $Ti^+(CH_3OH)_n$ cluster ions. This observation is consistent with the finding of El-Shall and co-workers[16] that the structure of the $Ti^+(OCH_3)_2(CH_3OH)_4$ ion can be regarded as an octahedral geometry involving a core $Ti^{3+}$ ion with two covalently bonded $OCH_3^-$ ligands. The evidence for this geometry is addressed later in this paper.

To unambiguously identify the product ions formed from the intracluster ion−molecule reactions of $Ti^+(CH_3OH)_n$, we performed the mass assignment for the low-mass region. Figure 3 shows a detailed view of the TOF mass spectrum for cluster ions smaller than $Ti^+(CH_3OH)_4$. The dominant cluster ions consist of a series of heterocluster ions $Ti^+(OCH_3)_m(CH_3OH)_n$ ($m = 1-3$ and $n = 0-3$) produced from the intracluster ion−molecule reactions, where $OCH_3$ is thought to be covalently bonded to the titanium ion. These ions can be interpreted as the outcome of sequential H-elimination reactions.

$$[Ti^+(CH_3OH)_n]^\ddagger \rightarrow Ti^+(OCH_3)(CH_3OH)_{n-1} + H \quad (4)$$

$$\rightarrow Ti^+(OCH_3)_2(CH_3OH)_{n-2} + 2H \quad (5)$$

$$\rightarrow Ti^+(OCH_3)_3(CH_3OH)_{n-3} + 3H \quad (6)$$

A surprising implication of this series of cluster reactions is that H-elimination in $CH_3OH$ by the $Ti^+$ ion is possible for up to three methanol molecules. This is consistent with the mass spectral data, which show peaks corresponding to the loss of one, two, or three mass units from the parent ion $Ti^+(CH_3OH)_n$ (denoted as $A_n$). With isotopically unsubstituted methanol, mass spectral measurements cannot distinguish between methoxide ($-OCH_3$) and hydroxymethyl ($-CH_2OH$) products, the former resulting from O−H cleavage, the latter from C−H cleavage. As discussed later, the isotope exchange experiments allow us to determine that the observed loss of a single mass unit arises from O−H bond cleavage.

As an alternative interpretation of the mass spectrum, it might be suggested that successive H-elimination reactions occur on a single methanol molecule, resulting in the products $Ti^+(CH_2O)$-

$(CH_3OH)_{n-1}$and $Ti^+(CHO)(CH_3OH)_{n-1}$. Sato and co-workers[15] observed the elimination of hydrogen molecules to give fragment complex ions $Ti^+(CH_2O)(CH_3OH)_{n-1}$, in addition to the formation of clustered complex ions $Ti^+(CH_3OH)_n$. An especially interesting question that arises in the reaction of $Ti^+$ with methanol is whether the $Ti^+$ ion abstracts three hydrogen atoms from the same methanol molecule or from three different methanol molecules within heteroclusters. If the *m*/*e* 141 peak (labeled with an asterisk, *) in Figure 3 corresponds to $Ti^+(CHO)(CH_3OH)_2$ instead of $Ti^+(OCH_3)_3$, for instance, ions with the cluster composition $Ti^+(CHO)$ and $Ti^+(CHO)(CH_3OH)$ should also be observed, considering that the cluster population decreases exponentially with its size. The total absence of such ions in the mass spectrum strongly implies that the $m/e = 141$ peak corresponds to the $Ti^+(OCH_3)_3$ ion. The observation of $Ti^+OCH_3$, $Ti^+(OCH_3)_2$, and $Ti^+(OCH_3)_3$ product ions along with their methanol complexes also support our conclusion that these cluster ions derive from sequential H-eliminations from the OH group of distinct $CH_3OH$ molecules, rather than from the $CH_3$ group of a single $CH_3OH$ molecule.

Further analysis of the mass spectrum reveals other reaction products with much smaller intensities. The observation of a mass peak corresponding to the $TiO^+$ ion is particularly intriguing. The formation of $TiO^+$ is not surprising in the sense that $Ti^+$ does form a very strong bond to oxygen atoms.[27] One might speculate that the $TiO^+$ ions arise from the Ti target materials we used. To clarify this question, pure Ar gas was expanded in the absence of methanol reactants. In the resulting mass spectrum, $Ti^+$ and $Ti^+Ar_n$ ($n = 1-20$) are the only ion signals and no other metal oxides or metal clusters are detected, demonstrating that $TiO^+$ ions are not produced from the oxide surface of the Ti target. In addition, when the $CH_3OH$ vapor is combined with the Ar carrier gas, a reproducible $TiO^+$ ion signal is observed during the repeated laser-ablation pulses on the Ti target. This also supports the suggestion that $TiO^+$ formation arises from the reaction of $Ti^+$ with methanol clusters. There are then two conceivable explanations for the formation of the $TiO^+$ ion, both arising from $Ti^+$ insertion into a C−O bond to form an $[HO-Ti^+-CH_3]$ intermediate. One explanation is that $TiO^+$ formation results from a four-centered elimination of $CH_4$ from this intermediate. A second explanation is that $TiO^+ + CH_4$ products arise from the intermediate by hydrogen migration to form an $O-Ti^+-CH_3(H)$ transition state, then by elimination of $CH_4$. A more detailed discussion is provided later in this paper. The observation of a relatively large peak in the mass spectrum corresponding to $TiO^+(OCH_3)(CH_3OH)_n$ (denoted as $Q_n$) indicates that the H-elimination reaction proceeds via intracluster reactions involving $TiO^+$ and methanol clusters.

The isotope substitution experiments with deuterated methanol provide additional evidence that is important in understanding H-elimination within the heteroclusters. We employed $CH_3OD$ in order to resolve overlapping ion peaks with the same mass but different chemical composition, such as in the case of the peaks for $TiOH^+$ and $(CH_3OH)_2H^+$ ions in the mass spectrum of Figure 3. Study of $Ti^+$ reactions with $(CH_3OD)_n$ also enables us to determine if the peaks appearing at multiple mass units lighter than the parent ion are from the loss of multiple H atoms from the $CH_3$ group or from sequential D-eliminations of OD groups within the heteroclusters. The mass spectrum for the reactions of $Ti^+$ with $(CH_3OD)_n$ obtained with a laser pulse energy of 15 mJ/cm$^2$ and an argon stagnation pressure of 1 atm is presented in Figure 4. Our data clearly show the 2 amu spacing between the $Ti^+(OCH_3)(CH_3OD)_{n-1}$, $Ti^+(OCH_3)_2(CH_3OD)_{n-2}$, and $Ti^+(OCH_3)_3(CH_3OD)_{n-3}$ peaks, which can only correspond to O−D cleavages from the association complex $Ti^+(CH_3OD)_n$. This result is in good agreement with the data of Lu and Yang,[28] who claim that the hydrogen atom elimination channel of $Mg^+$ with methanol clusters leads to product ions with apparent stoichiometry $MgOCH_3{}^+(CH_3OH)_n$. In addition, the formation of $Ti^+(OCH_3)_3(CH_3OD)_n{}^+$ ions also supports our previous conclusion that H-elimination due to the $Ti^+$ ion occurs from separate methanol molecules.

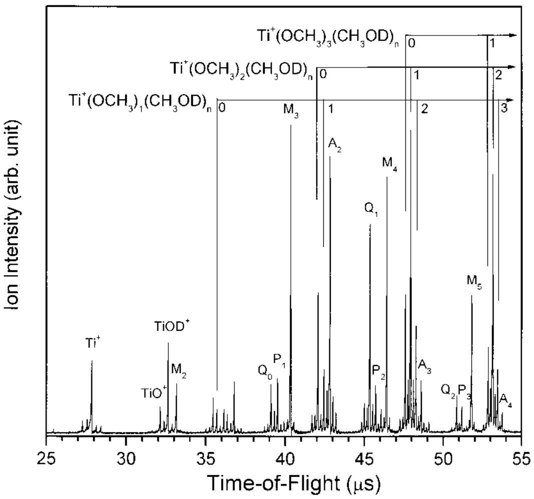


**Figure 4.** Time-of-flight mass spectrum showing the product ions in the low-mass region from the reactions of $Ti^+$ with $(CH_3OD)_n$ seeded in 1 atm Ar: $A_n$, $Ti^+(CH_3OD)_n$; $M_n$, $(CH_3OD)_nD^+$; $P_n$, $TiO^+(CH_3OD)_n$; $Q_n$, $TiO^+(OCH_3)(CH_3OD)_n$. The laser fluence is 15 mJ/cm$^2$.

The $TiOD^+$ formation channel is clearly observed in the $CH_3OD$ system, while $^{48}TiOH^+$ ($m/e = 64.9479$) and $(CH_3OH)_2H^+$ ($m/e = 65.0447$) ions are difficult to distinguish due to their almost identical masses when $CH_3OH$ clusters are employed (see Figure 3). The formation of $TiOD^+$ ion is primarily attributable to the $CH_3$ elimination reaction from the $[DO-Ti^+-CH_3]$ intermediate formed by $Ti^+$ insertion into a C−O bond in a methanol molecule. The formation of metal hydroxide ions from methanol has been observed in other metal ion systems, including $Mg^+$,[29] $Fe^+$,[30] and $Sr^+$,[31] coinciding with the elimination of $CH_3$. Since the $CH_3-OH$ bond energy is 92.4 kcal/mol [21] and the binding energy of $Ti^+-OH$ is 111.1 kcal/mol,[32] we estimate that the ground-state reaction for $Ti^+ + CH_3OH \rightarrow Ti^+-OH + CH_3$ is exothermic by 18.7 kcal/mol. This is consistent with recent results for the reactions of alkaline earth metal ions with methanol, which show exothermic reactions that readily occur in the gas phase.[33] Further, it is noted that peaks corresponding to $TiO^+(CH_3OD)_n$ and $TiO^+(OCH_3)(CH_3OD)_n$ ions (labeled as $P_n$ and $Q_n$, respectively) also emerged with negligible isotope contribution from the neighboring peaks. This result indicates that $TiO^+$ formed from the ion−molecule reaction $Ti^+ + CH_3OH$ can undergo subsequent H-elimination reactions with methanol within the clusters.

To investigate the solvent effect of argon atoms on the abundance distribution of heterocluster ions, the mass spectrum was taken at different stagnation pressures. Figure 5 shows the mass spectra obtained when neat methanol (125 Torr) is expanded or seeded in argon buffer gas. Each spectrum covers the same mass range, which has been chosen to show peaks corresponding to $Ti^+(OCH_3)_m(CH_3OH)_n$ clusters ($7 \le m + n \le 9$). When methanol vapor seeded in 1 atm argon is expanded (Figure 5b), the H-, 2H-, and 3H-elimination products are observed, with the 2H-elimination process dominant. As the argon stagnation pressure is increased, however, the solvation

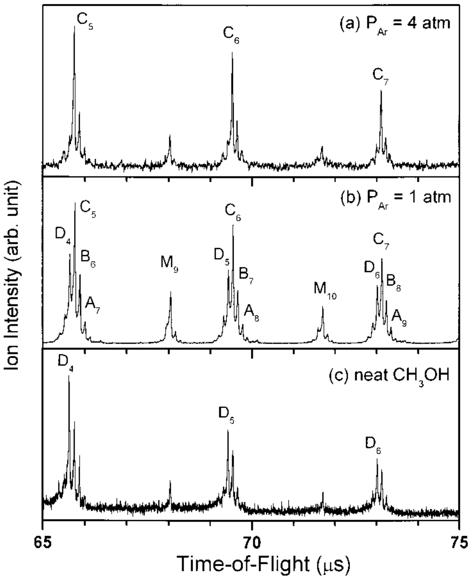


**Figure 5.** Time-of-flight mass spectra at different stagnation pressures of (a) 4 atm Ar, (b) 1 atm Ar, and (c) neat $CH_3OH$: $A_n$, $Ti^+(CH_3OH)_n$; $B_n$, $Ti^+(OCH_3)(CH_3OH)_n$; $C_n$, $Ti^+(OCH_3)_2(CH_3OH)_n$; $D_n$, $Ti^+(OCH_3)_3(CH_3OH)_n$.

of $Ti^+$ ions by neutral methanol molecules becomes unfavorable, due to the lower percentage of methanol in the $CH_3OH$/Ar mixture. At 4 atm pressure, the overall spectral pattern is different from that at low stagnation pressure. $Ti^+(OCH_3)_3(CH_3OH)_n$ ions (labeled as $D_n$) are substantially decreased in abundance, whereas the same ions show a considerable contribution compared with the $Ti^+(OCH_3)(CH_3OH)_n$ (labeled as $B_n$) and $Ti^+(OCH_3)_2(CH_3OH)_n$ (labeled as $C_n$) species at low Ar stagnation pressure. This observation is easily explained by the solvent effect of the noble gas. In general, at high stagnation pressure there are more argon atoms than methanol molecules in the heterocluster and the reaction probability of the $Ti^+$ ion with methanol is greatly suppressed by the argon moiety. The effective cooling of heterocluster ions formed from the supersonic jet at high stagnation pressure would also contribute to the decreased chemical reactivity. With an expansion of neat methanol vapor in the absence of Ar gas, a very distinctive feature appears, as shown in Figure 5c. The methanol molecules solvating around the $Ti^+$ ion have a higher chance of reacting with the $Ti^+$ ion, resulting in a greatly enhanced peak corresponding to $Ti^+(OCH_3)_3(CH_3OH)_n$ ions in the mass spectrum. Therefore, the present results strongly suggest that H-elimination reactions are highly dependent on the methanol concentration within the clusters.

To shed more light on the variation of the reactivity of the $Ti^+$ ion with cluster size, we investigated the general trends in the ion abundance distributions of heteroclusters. Figure 6 shows two regions (85−91 and 102−107 μs) of a typical mass spectrum for the reaction of $Ti^+$ with $(CH_3OD)_n$ clusters. The mass resolution in this high-mass region is slightly low, but is still high enough to distinguish differences of one atomic mass unit between the cluster ions. As observed in the mass spectra discussed above, and in the low-mass region of Figure 6, the intensities of $Ti^+(CH_3OD)_n$ cluster ions are much lower than those of $Ti^+(OCH_3)_2(CH_3OD)_{n-2}$ cluster ions, and this trend is maintained for all $n \leq 16$. The pronounced formation of $Ti^+(OCH_3)_2(CH_3OD)_{n-2}$ ions for small cluster sizes can be interpreted as the extensive evaporation (i.e. boil-off), of weakly bound methanol molecules from the exterior of the cluster. This evaporation is a result of the excess energy available from the exothermicity of the intracluster ion−molecule reactions.

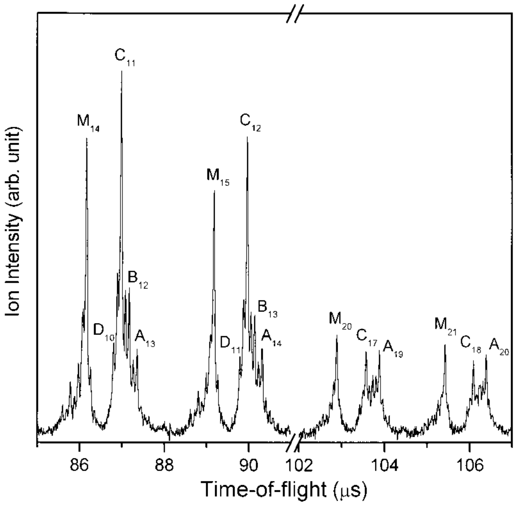


**Figure 6.** Time-of-flight mass spectrum showing two regions of the cluster ions produced by reactive collision of laser-ablated $Ti^+$ and $CH_3OD$ clusters seeded in 1 atm Ar: $A_n$, $Ti^+(CH_3OD)_n$; $M_n$, $(CH_3OD)_nD^+$; $C_n$, $Ti^+(OCH_3)_2(CH_3OD)_n$; $D_n$, $Ti^+(OCH_3)_3(CH_3OD)_n$.

As the cluster size increases, however, the intensities of $Ti^+(CH_3OD)_n$ cluster ions become comparable with those of $Ti^+(OCH_3)_2(CH_3OD)_{n-2}$ ions. This phenomenon, known as “product switching”, was observed in a study of the reactions $Mg^+ + (H_2O)_n$, where for $n \geq 15$ $Mg^+(H_2O)_n$ is the dominant species, with only very small quantities of the $Mg^+(OH)(H_2O)_{n-1}$ series present.[34] These results show that the reactivity of the $Ti^+$ ion diminishes with increasing solvation by methanol molecules. This apparent quenching of H-elimination reactions is attributed to increased stabilization of $Ti^+(CH_3OH)_n$ cluster ions with an increase in the degree of solvation. Another possibility is that the methanol molecules surrounding the metal ion create an energy barrier in the reaction pathway for H-elimination. Because the capability of hydrogen atom transport after O−H bond cleavage is greatly reduced within such a tightly packed solvent cage, the trapping probability of hydrogen atom eliminated from $CH_3OH$ is expected to increase with increasing cluster size.[28] The consequence is that H-elimination reactions may be suppressed in sufficiently large clusters.

## IV. Discussion

The intracluster reaction of $Ti^+(CH_3OH)_n$ appears to have three elimination channels open: H-, $CH_3$-, and $CH_4$-elimination, with H-elimination predominating. There are three types of chemical bonds (C−H, C−O, and O−H) in a methanol molecule that might permit the insertion of an $Ti^+$ ion. The enthalpies of the possible ion−molecule reactions, estimated from the thermochemical data,[21,35,36] are listed in Table 1. First, if C−H bond insertion takes place and the $[H-Ti^+-CH_2OH]$ intermediate is formed, $TiH^+$ and $Ti^+(CH_2OH)$ ions are expected to be produced through $Ti^+-C$ and $Ti^+-H$ bond dissociations, respectively. However, the absence of product ions corresponding to $TiD^+$ and $Ti^+(CH_2OD)$ in the deuterium isotope experiments with $CH_3OD$ indicates that the C−H insertion process does not occur within the heteroclusters. This result is consistent with the high endothermicity (39.7 and 36.4 kcal/mol for $Ti^+-H$ and $Ti^+-CH_2OH$ formation channels, respectively) of the C−H insertion reaction.

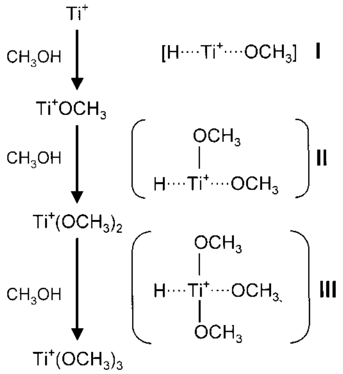
A second possibility comes from the C−O insertion reaction of the $Ti^+$ ion, producing $TiOH^+$ and $TiO^+$ ions, which are in

**TABLE 1: Energetics of Possible Reaction Pathways for $Ti^+$ + $CH_3OH$[a]**

| insertion site | reacn products | enthalpy (kcal/mol) |
|---|---|---|
| C–H Bond | $\rightarrow Ti^+{-}H + CH_2OH$ | 39.7 |
| | $\rightarrow Ti^+{-}CH_2OH + H$ | 36.4[b] |
| C–O Bond | $\rightarrow Ti^+{-}CH_3 + OH$ | 34.9 |
| | $\rightarrow Ti^+{-}OH + CH_3$ | 18.7 |
| | $\rightarrow Ti^+{-}O + CH_4$ | 68.8 |
| O–H Bond | $\rightarrow Ti^+{-}H + OCH_3$ | 50.0 |
| | $\rightarrow Ti^+{-}OCH_3 + H$ | 6.9[c] |

[a] Reaction enthalpies are calculated from the thermochemical data provided in refs 21, 35, and 36. [b] The bond energy $D_0(Ti^+{-}CH_2OH)$ is assumed to equal $D_0(Ti^+{-}CH_3)$. [c] $D_0(Ti^+{-}OCH_3)$ is assumed to equal $D_0(Ti^+{-}OH)$.

**SCHEME 1**



fact observed in the present experiments. These reactions within the heterocluster ions are summarized by

$$Ti^+(CH_3OH) \rightarrow [HO{-}Ti^+{-}CH_3]^\ddagger$$

$$\rightarrow TiOH^+ + CH_3 \quad (7)$$

$$\rightarrow TiO^+ + CH_4 \text{ (or } CH_3 + H) \quad (8a)$$

The enthalpy changes of reactions 7 and 8a show exothermicities of 18.7 and 68.8 kcal/mol, respectively, suggesting that these reactions will appear as they become energetically feasible. The formation of $TiOH^+$ from the $[HO{-}Ti^+{-}CH_3]$ intermediate is plausible, because the enthalpy required for the bond dissociation of $Ti^+{-}CH_3$ (57.5 kcal/mol)[36] is much lower than that of $Ti^+{-}OH$ (111 kcal/mol).[32] The $TiO^+$ formation channel can proceed from the intermediate through a four-centered transition state, as Armentrout and co-workers have suggested.[14] The $TiO^+$ ion can also be produced from the $[HO{-}Ti^+{-}CH_3]$ intermediate by hydrogen transfer to the metal ion, forming $CH_4$, which is then lost as a neutral product. This mechanism is similar for the $Ti^+ + H_2O \rightarrow TiO^+ + H_2$ reaction, in which an $H_2Ti^+{-}O$ intermediate[12] can form because $Ti^+$ has three valence electrons. However, the fact that only minor contributions from $TiO^+$ and $TiOH^+$ ions are evident in the mass spectra demonstrates that the insertion reaction of $Ti^+$ into the C–O bond is less efficient than other pathways among the intracluster ion–molecule reactions.

Finally, as a major reaction channel, we suggest that the $Ti^+$ ion can insert into the O–H bond of a methanol molecule.

$$Ti^+(CH_3OH) \rightarrow [H{-}Ti^+{-}OCH_3]^\ddagger \rightarrow TiO^+ + CH_4 \quad (8b)$$

$$\rightarrow Ti^+(OCH_3) + H \quad (9)$$

The formation of the $TiH^+$ ion via $Ti^+{-}OCH_3$ bond rupture is unfavorable due to the relatively low dissociation energy (54.2 kcal/mol)[36] of the Ti–H bond. $TiO^+$ formation from reaction 8b is similar to that from reaction 8a, as mentioned above. The present mass spectral data alone are insufficient to assign the formation mechanism of $TiO^+$ unequivocally to reaction 8a or 8b. The lesser intensity of the $TiO^+$ ion peak in the mass spectrum, compared with those of the H-elimination products such as $Ti^+(OCH_3)_m(CH_3OH)_n$ clusters, implies that the $TiO^+$ ion is not produced from an O–H insertion reaction. In this regard, we suggest that reaction 8a prevails over reaction 8b.

By considering methanol bond strengths, Armentrout and co-workers[37] have shown that C–H collisional activation is both energetically and statistically favored over activation of the O–H bond in $CH_3OH$; breaking the O–H bond requires 10.3 kcal/mol more energy than breaking the C–H bond. The thermodynamic data also show that the $CH_3{-}OH$ bond dissociation energy is 92.4 kcal/mol, which is less than that of the $CH_3O{-}H$ bond (104.2 kcal/mol). Thus C–H and C–O bond insertion reactions seem more energetically favorable than the O–H insertion reaction. Yet despite the large O–H bond dissociation energy, it is this H-elimination that is observed to predominate in the present experiments. One possible rationale for our result is that the breakage of the O–H bond in $CH_3OH$ is compensated for by the formation of a $Ti^+{-}OCH_3$ bond. The binding energy of $Ti^+{-}OCH_3$ is not yet available. However, considering that $CH_3$ is more polarizable than H and that this polarizability would increase the ligand contribution to the bonding,[38] we expect that the binding energy for $Ti^+{-}OCH_3$ should be larger than that of $Ti^+{-}OH$ (111 kcal/mol). Thus, although the $CH_3O{-}H$ bond dissociation energy is 11.8 kcal/mol larger than that of $CH_3{-}OH$, the large bond dissociation energy of $Ti^+{-}OCH_3$ may still make the H-elimination reaction exothermic.

A surprising finding for $Ti^+(OCH_3)(CH_3OH)_n$ cluster ions is that they can further dehydrogenate to give $Ti^+(OCH_3)_3(CH_3OH)_n$. For the observed cluster ions $Ti^+(OCH_3)_m(CH_3OH)_n$ ($1 \leq m \leq 3$), we propose the consecutive reaction mechanism outlined in Scheme 1.

Within the stabilizing environs of a heterocluster, the reaction is initiated by $Ti^+$ insertion into an O–H bond of the solvating methanol molecule to form the intermediate **I**. This intermediate may now dissociate internally, and $Ti^+(OCH_3)$ ion is produced via H-elimination, with the $OCH_3$ group behaving more like a tightly bound group than a solvating ligand species. It has been found that the binding energies of $Mg^+{-}OCH_3$ (67.35 kcal/mol)[28] and $Co^+{-}OCH_3$ (>69 kcal/mol)[36] are much stronger than those of $Mg^+{-}CH_3OH$ (37.7 kcal/mol) and $Co^+{-}CH_3OH$ (35.28 kcal/mol). Bonding in the $Ti^+OCH_3$ ion is thus likely to resemble covalent binding rather than electrostatic. Similarly, further insertion of a $Ti^+OCH_3$ ion into a second methanol molecule, followed by H-elimination, results in the formation of $Ti^+(OCH_3)_2$. Around the $Ti^+(OCH_3)_2$ ion, there is room for one additional methanol molecule, forming intermediate **III**. An abrupt decrease in the number of cluster ions with formula $Ti^+(OCH_3)_m(CH_3OH)_n$ occurs for $m \geq 4$, which reflects the fact that the coordination of three $OCH_3$ groups around a $Ti^+$ ion leads to a great reduction in the reactivity of $Ti^+$ with respect to breaking the O–H bond of additional methanol molecules. Because the $Ti^+$ ion has three valence electrons, this decrease is primarily attributable to the large binding energy change that is caused when trivalent bond formation is completed by three ligands with methoxy groups This interpretation is consistent with the tetrahedral structures commonly observed for stable compounds such as $TiCl_4$ and $Ti(OCH_3)_4$.

As another possible route to produce $Ti^+(OCH_3)_m(CH_3OH)_n$ ($1 \leq m \leq 3$) ions, $Ti^+(OCH_3)_2(CH_3OH)_n$ products might come

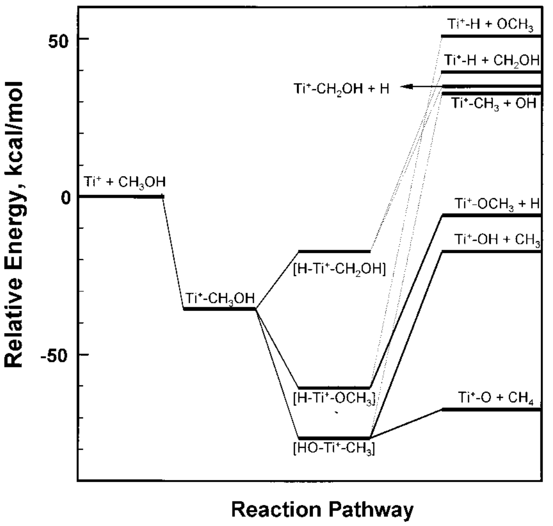


**Figure 7.** Schematic energy diagram for the ion−molecule reactions of $Ti^+$ and $CH_3OH$. Thermochemical data were obtained from refs 21, 34, and 35.

from the reaction of ground-state $Ti^+$ to cause $H_2$ elimination while the odd-methoxy products arise by reaction of excited-state $Ti^{+*}$ in the beam. Evidently $Ti^{+*}$ gives $TiOH^+$ from the enhanced reactivity with water.[35] The analogous reaction gives the $Ti^+(OCH_3)(CH_3OH)_n$ products. The $Ti^+(OCH_3)_3(CH_3OH)_n$ products are then the result of second step along this path, arising from subsequent elimination of an additional $H_2$ molecule. Elimination of $H_2$ products is far more exothermic than loss of H atom. Certainly the methanol molecules complexed to $Ti^+$ will orient their oxygen atoms toward the metal ion. To produce $H_2$, ground-state $Ti^+$, with only three valence electrons, might simultaneously insert into two OH bonds of two different methanol molecules. This would be somewhat analogous to the multicenter transition state in the $Ni^+ + C_4H_{10}$ reaction pathways, discovered by Weisshaar and co-workers.[39] After central CC insertion to form $Ni^+(C_2H_5)_2$, two H atom simultaneously migrate to the $Ni^+$ ion to form incipient $H_2$ products. The $Ti^+$ + methanol reaction would be a similar example.

Figure 7 shows a schematic energy diagram representing the reaction pathways of $Ti^+ + CH_3OH$, which was constructed from the calculated thermochemical data. This diagram provides a useful guide to the reaction energetics of the heterocluster systems explored in the present work. The electronic state of the $Ti^+$ ion that correlates with the reaction products is the $a^4F(3d^24s)$ state, the lowest quartet state having an s electron.[36] Recent studies have shown that the reactions of metal ions with molecules are affected by the electronic state and kinetic energy of the metal ion. Armentrout and co-workers[35] studied the reaction of $Ti^+$ with $D_2O$ and found that the excited $a^2F$ state of $Ti^{+*}$ reacts much more efficiently than the $a^4F$ ground state in forming the $TiD^+$, $TiO^+$, and $TiOD^+$ product ions. They attribute the enhanced reactivity of the excited $a^2F$ state to electron spin conservation throughout the potential energy surface rather than to differences in activation barriers. In this regard, other low-lying states such as $b^4F$ and $a^2D$ may also participate in the ion−molecule reactions.

While we cannot exclude all possible reactions by electronically excited $Ti^+$ ions, we believe that the observed reaction patterns in the current experiments are mainly due to ground-state reactions. This is because the laser-ablated $Ti^+$ ions are likely to be efficiently quenched by their collision with the supersonic beam of $CH_3OH$/Ar, though it is hard to estimate the number of collisions. Similarly, it has been found that excited-state $Ti^+$ ions are cooled translationally and quenched electronically by collisions when $Ti^+$ ions from an electron impact source are passed through a drift cell filled with a gas at high pressure.[36] In addition, the failure to observe any reaction products from the endothermic reaction channels even at high laser fluence supports our hypothesis that $Ti^+$ ions in high-lying states make no appreciable contribution to the H-, $CH_3$-, and $CH_4$-elimination reactions.

The broad distribution of the kinetic energy of the laser-ablated $Ti^+$ ions may also influence the observed reaction patterns. In a guided ion beam study of $Ti^+ + D_2O$ reactions, it has been reported that the formation of $TiO^+ + D_2$ is the dominant process at low energy, presumably due to its high exothermicity (−40.8 kcal/mol) compared with the endothermic $TiD^+ + OD$ (+66.2 kcal/mol) and $TiOD^+ + D$ (+9.0 kcal/mol) channels.[35] However, the $TiD^+$ product channel becomes dominant at high energy, which is typical behavior for the reaction of atomic metal ions with H- and D-containing polyatomic molecules.[36,40] Nevertheless, we have good reason to believe that the product ions observed in the present experiments are those resulting from $Ti^+$ ions with very low kinetic energy. One would expect that the kinetic energy of $Ti^+$ ions would be greatly reduced by collisional quenching with argon carrier gas, resulting in the production and detection of relatively stable clustered product ions. Much of the kinetic energy may also be dissipated by solvent evaporation of methanol molecules from the clusters. This is consistent with the present observation that the chemical reactivity of the $Ti^+$ ion diminishes with an increasing degree of $CH_3OH$ solvation. Further, product ions formed from high kinetic energy $Ti^+$ ions will have a large momentum along the laser-ablation axis and so cannot enter the ion extraction region of TOF mass spectrometer. Thus the cluster ions sampled in the present experimental apparatus correspond to those originating preferentially from relatively low-energy $Ti^+$ ions.

As displayed in Figure 7, it is noteworthy that the ion−molecule reactions leading to the formation of $TiO^+$, $TiOH^+$, and $Ti^+OCH_3$ ions show rather large exothermicity, indicating that these are the energetically feasible reactions, as discussed above. At long range, the interaction between $Ti^+$ and $CH_3OH$ species can be considered an ion−dipole attraction. Thus, a well corresponding to the $Ti^+-CH_3OH$ complex is presumed. The binding energy of $CH_3OH$ to $Ti^+$ has not been measured or calculated, but an approximate estimate is ∼35 kcal/mol based on the similarity between the binding energies of metal ion−molecules such as $Ti^+-C_3H_6$ (34.5 kcal/mol),[41] $Ti^+-H_2O$ (36.9 kcal/mol),[42] $Co^+-H_2O$ (37.1 kcal/mol),[43] $Co^+-CH_3OD$ (35.3 kcal/mol),[37] and $Mg^+-CH_3OH$ (37.7 kcal/mol).[28]

$Ti^+$ insertion into the C−H, C−O, and O−H bonds of a methanol molecule can lead to three intermediates. The formation energies of $[H-Ti^+-CH_2OH]$, $[HO-Ti^+-CH_3]$, and $[H-Ti^+-OCH_3]$ intermediates are estimated to be −17.7, −76.0, and −61.1 kcal/mol, respectively, based on the bond additivity assumption that the bond energy $D_0(Ti^+-CH_2OH) \approx D_0(Ti^+-CH_3)$ and $D_0(Ti^+-OCH_3) \approx D_0(Ti^+-OH)$. Although this assumption may not be quantitatively accurate, it is the only reasonable means for estimating the energy of the three possible intermediates. The intermediate $[H-Ti^+-CH_2OH]$ can decompose to form $Ti^+-H + CH_2OH$ and $Ti^+-CH_2OH + H$ by simple bond fissions of the Ti−C and Ti−H bonds, respectively. However, both product channels are then thermodynamically unfavorable due to their high endothermicity, which is consistent with the present experiments. In addition to activation of the $H-CH_2OH$ bond, the $Ti^+$ ion can also activate the $CH_3O-H$

or $CH_3-OH$ bond of the $CH_3OH$ molecule to form the $[H-Ti^+-OCH_3]$ or $[HO-Ti^+-CH_3]$ intermediates. Because $Ti^+-OCH_3$ is the predominant ionic product observed in the present experiments, it is likely that the $Ti^+$ insertion into the O−H bond to form the $[H-Ti^+-OCH_3]$ intermediate is the most favored reaction channel of the three possible routes. The dominance of the $Ti^+-OCH_3 + H$ product channel over the $Ti^+-H + OCH_3$ channel can be rationalized on the basis that a $Ti^+-OCH_3$ bond is stronger than a $Ti^+-H$ bond. In contrast to the $Ti^+-OCH_3 + H$ product channel, formation of $Ti^+-OH + CH_3$ or $Ti^+-O + CH_4$ from the $[HO-Ti^+-CH_3]$ intermediate does not play a significant role despite its high exothermicity. We attribute the difference in importance of the two intermediates, $[H-Ti^+-OCH_3]$ and $[HO-Ti^+-CH_3]$, to a difference in activation barriers for the subsequent elimination. The $[HO-Ti^+-CH_3]$ intermediate might efficiently eliminate $CH_3$ and $CH_4$ because these channels are thermodynamically much more favorable. However, our observation that $Ti^+-OH$ and $Ti^+-O$ formation channels are less favorable than the $Ti^+-OCH_3$ formation channel suggests that there exists a considerable barrier between the $[HO-Ti^+-CH_3]$ intermediate and elimination of $CH_3$ and $CH_4$.

## V. Conclusion

Reactions that proceed within mixed titanium−methanol cluster ions were studied using the laser ablation-molecular beam method. The $Ti^+$ ions are produced by the laser ablation of a rotating metal target at 355 nm and allowed to react with methanol clusters in an injected molecular beam. The primary reaction of $Ti^+$ ions with methanol clusters appears to have three open elimination channels: H-, $CH_3$-, and $CH_4$-eliminations, with H-elimination being the dominant process. In studies on the origin of the hydrogen elimination, isotope-labeling experiments led us to conclude that insertions of the $Ti^+$ ion into the O−H bond of a methanol molecule within the heteroclusters play an important role in producing $Ti^+(OCH_3)_m(CH_3OH)_n$ ions ($1 \le m \le 3$). In addition, it is found that the $Ti^+$ ion can induce H-elimination from up to three methanol molecules. This result is interpreted to be a consequence of consecutive insertion reactions of the $Ti^+$ ion within the heteroclusters, leading to the formation of $Ti^+(OCH_3)_3(CH_3OH)_n$ ions. The observation of $TiOH^+$ and $TiO^+$ ions is understood on the basis of a C−O insertion reaction followed by fragmentation. It is also found that intracluster ion−molecule reactions are greatly influenced by cluster size and the pressure of the argon carrier gas. The chemical reactivity of $Ti^+$ ions within the heteroclusters decreases with increasing cluster size and increasing argon stagnation pressure. The reaction pathways and energetics of the proposed mechanisms have been presented.

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