

Chemical Reactivity of Ti^+ within Water, Dimethyl Ether, and Methanol Clusters

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The intracluster ion-molecule reactions of $\text{Ti}^+(\text{H}_2\text{O})_n$, $\text{Ti}^+(\text{CH}_3\text{OCH}_3)_n$, and $\text{Ti}^+(\text{CH}_3\text{OD})_n$ complexes produced by the mixing of the laser-vaporized plasma and the pulsed supersonic beam were studied using a reflectron time-of-flight mass spectrometer. The reactions of Ti^+ with water clusters were dominated by the dehydrogenation reaction, which produces $\text{TiO}^+(\text{H}_2\text{O})_n$ clusters. The mass spectra resulting from the reactions of Ti^+ with CH_3OCH_3 clusters exhibit a major sequence of $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OCH}_3)_n$ cluster ions, which is attributed to the insertion of Ti^+ ion into C-O bond of CH_3OCH_3 followed by CH_3 elimination. The prevalence of $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OD})_n$ ions in the reaction of Ti^+ with CH_3OD clusters suggests that D elimination *via* O-D bond insertion is the preferred decomposition pathway. In addition, the results indicate that consecutive insertion reactions by the Ti^+ ion occur for up to three precursor molecules. Thus, examination of Ti^+ insertion into three different molecules establishes the reactivity order: O-H > C-O > C-H. The experiments additionally 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.

Key Words : Cluster, Ion-molecule reaction, Titanium, TOF mass spectrometry

Introduction

Chemical reactions induced by the interaction of transition metal ions with various molecules have been studied extensively in order to elucidate the catalytic activity of metal ions, which is important in a wide range of areas of chemistry including heterogeneous and homogeneous catalysis, inorganic chemistry, and biochemical processes.¹⁻⁴ Mass spectrometric studies of gas-phase ion-molecule reactions have also provided information about the bimolecular chemistry of ions with neutral molecules in the absence of complicating solvent phenomena.⁵ Such gas-phase studies have provided insights into the intrinsic chemical and physical properties of transition metal ions, and these insights have enhanced our understanding of the behavior of transition metal ions in the condensed phase.

Studies of the reactions of Ti^+ with small alkane molecules have revealed that Ti^+ is very active in the breaking of C-H bonds, leading to the dehydrogenation of the alkanes.⁶⁻⁹ The alkanes were found 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.¹⁰ In studies of the reaction of Ti^+ with water using selected ion drift tube technique¹¹ and guided ion beam tandem mass spectrometry,¹² it has been reported the primary reaction channel proceeds by Ti^+ insertion into the O-H bond to form H-Ti⁺-OH intermediate, which then loses H_2 to produce TiO^+ . Other experiments on the gas-phase ion-molecule reactions of Ti^+ with a series of ketones, aldehydes, ethers, and esters have shown that Ti^+ extracts an oxygen atom from small carbonyl compounds

and cyclic ethers to form TiO^+ .¹³ However, the reactions of Ti^+ with organic molecules remain a subject of much debate, with unresolved issues concerning fundamental mechanistic details such as the relative reactivity of Ti^+ toward insertion and elimination reactions, and the structures surrounding this ion under solvation conditions.

Although the products of gas-phase ion-molecule reactions have been extensively investigated, few studies have examined the chemical reactions taking place within the heterocluster ion itself. The product distribution of metal ion-solvent heteroclusters provides valuable information on the changes in the reaction pathways with increasing cluster size, which reflects the transition from gas-phase to solution-phase reactions. Also of interest are the specific chemical dynamics of reactions within cluster ions, on account of their potential as models for surface reactions and heterogeneous catalysis.¹⁴⁻¹⁷ Thus, the dependence of the reactivity of heteroclusters on cluster size is a fascinating and intriguing issue.

In this work, we extend our earlier study of the Ti^+ -methanol heterocluster system,¹⁸ in which we investigated the reactivity of Ti^+ with respect to the breaking of the C-H, C-O, and O-H bonds in H_2O , CH_3OCH_3 , and CH_3OD molecules. The principal aim of the present work is to develop a quantitative interpretation of the reaction mechanisms behind our previous observations. In order to probe the cluster reactivity, we examined the reactions using a combination of laser vaporization and supersonic gas expansion. The present results provide further details on the intracluster reactions in heterocluster systems and thermochemical data for enthalpies of reaction. Studies of the reactivity of titanium-dimethyl ether heteroclusters as a function of Ar stagnation pressure

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and cluster size also aid the understanding of the influence of solvation on reactions within clusters and the nature of the CH_3 elimination reactions of the Ti^+ ion on a molecular level.

Experimental Section

A detailed description of the laser vaporization-molecular beam/reflectron time-of-flight mass spectrometer (RTOFMS) has been given previously.¹⁸ Below we present a brief summary of the technique employed. Reactant clusters of water, dimethyl ether, or methanol were formed *via* the adiabatic expansion of a mixture of the target molecule with argon through a pulsed nozzle in the source chamber. After opening the solenoid valve, the third harmonic (355 nm) of a Nd:YAG laser struck the rotating Ti target (99.999%, Goodfellow) located 2 cm downstream from the nozzle. The laser radiation was focused using a 35-cm focal length lens to a spot size of $\leq 1 \text{ mm}^2$. The laser fluence at the target surface was varied in the range 10–100 mJ/cm^2 . Under the relatively low power density utilized in these experiments, the plasma consisted of monatomic ionic and neutral species. The laser-vaporized metal ions perpendicularly crossed the expansion stream 1 cm from the target, where they reacted with the reactant clusters. The ion complexes were then skimmed by a skimmer of diameter 1 mm and cooled collisionally as they traveled through the detection region. The distance between the nozzle and skimmer was 4 cm. The resulting pulsed beam entered the extraction region of a RTOFMS, which was placed 10 cm downstream of the nozzle. Under normal operating conditions, the pressures in the source and detection chambers were always below 3×10^{-5} and 5×10^{-7} Torr respectively.

Following a delay of typically 50–200 μs after the laser irradiation, the positive ions were extracted by a +2200 V pulsed electric field, applied to the repeller. The delay times between the valve opening, laser firing, and ion extraction pulse were adjusted to obtain the maximum signal intensities of the heteroclusters. The accelerated ions then traveled through a field-free region of length 1 m, which terminated at a double stage reflectron (R.M. Jordan Co.) located at the end of the flight tube. From the reflectron, the ions traveled an additional 64 cm back to a chevron microchannel plate detector. The signal from the detector was sent to a digital storage oscilloscope (LeCroy LT322, 500 MHz) where it was typically averaged over 1000 shots and further processed on a computer. Spectrophotometric grade H_2O (99.9%), CH_3OCH_3 (>99%), and CH_3OD (>99.5% D) (Aldrich Chemical) were used after further purification through a series of freeze-pump-thaw cycles to remove dissolved atmospheric gases and other impurities of high vapor pressure.

Results

Figure 1 displays a typical mass spectrum resulting from the reaction of Ti^+ with H_2O clusters. The spectrum was obtained using a laser pulse energy of 40 mJ/cm^2 and an argon stagnation pressure of 2 atm. We observe pentads of

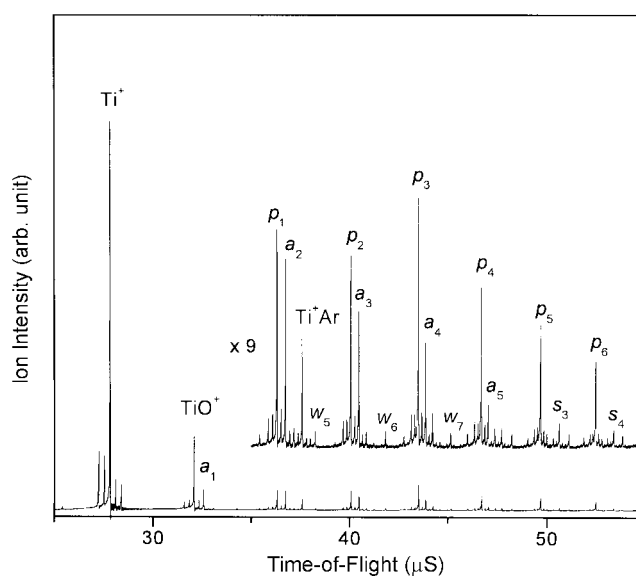
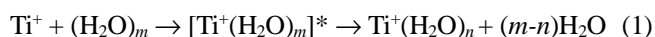


Figure 1. Time-of-flight mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti^+ and water clusters seeded in 2 atm Ar. The laser fluence is 40 mJ/cm^2 . a_n : $\text{Ti}^+(\text{H}_2\text{O})_n$; p_n : $\text{TiO}^+(\text{H}_2\text{O})_n$; s_n : $\text{TiO}_3^+(\text{H}_2\text{O})_n$; w_n : $(\text{H}_2\text{O})_n\text{H}^+$.

peaks corresponding to the natural abundances of the isotopes of titanium (^{46}Ti , 8.0%; ^{47}Ti , 7.3%; ^{48}Ti , 73.8%; ^{49}Ti , 5.5%; ^{50}Ti , 5.4%).¹⁹ Unless otherwise noted, the results presented below refer to complexes involving the most abundant isotope. In addition to the protonated water clusters (labeled w_n), the mass spectrum exhibits a major sequence of heterocluster ions of formula $\text{TiO}^+(\text{H}_2\text{O})_n$ (labeled p_n). These heteroclusters can be attributed to an oxidation or dehydrogenation reaction within the parent $\text{Ti}^+(\text{H}_2\text{O})_n$ (labeled a_n) cluster ions to form titanium oxide clusters. The intact cluster ions $\text{Ti}^+(\text{H}_2\text{O})_n$ stem from the association reaction between Ti^+ and water clusters, possibly followed by evaporation of water molecules:



The evaporation of H_2O results from the excess kinetic energy of the Ti^+ ions and also from the exothermicity of the ion-molecule association reactions. From the viewpoint of the ionization energies (IEs), the positive charge should be localized on the Ti atom (IE = 6.82 eV) because its IE value is substantially lower than that of the water molecule (12.62 eV). Evidence supporting this claim has been provided by several beam experiments on the formation of the metal ion-organic molecule or metal ion-rare gas clusters.^{20,21}

The dehydrogenation reaction within a $\text{Ti}^+(\text{H}_2\text{O})_n$ cluster ion can be expressed as follows:



A reaction of this type has been recently observed in a gas phase ion-molecule reaction of Ti^+ with H_2O at thermal energies.¹¹ The formation of TiO^+ is not surprising given the fact that Ti^+ forms very strong bonds with oxygen atoms.²² One might speculate that the TiO^+ ions arise from the Ti target. Prior to the seeding of the H_2O vapor, pure Ar gas was

expanded to inspect the ion products from the ion source. The only ion signals in the resulting mass spectrum were those of Ti^+ and Ti^+Ar_n ($n = 1-20$), with no evidence of other metal oxides or metal clusters, demonstrating that TiO^+ ions are not produced from the Ti target. In addition, when the water vapor was combined with the Ar carrier gas, a reproducible TiO^+ ion signal was observed during the repeated laser-vaporization pulses on the Ti target. This provides additional support for the suggestion that TiO^+ forms through the reaction of Ti^+ with water clusters.

The observation in the mass spectrum of a sequence corresponding to ions of formula $\text{TiO}_3^+(\text{H}_2\text{O})_n$ (labeled s_n) is particularly intriguing. This implies that TiO^+ ion produced in reaction 2 reacts further in sequential dehydrogenation reactions with H_2O molecules to form TiO_3^+ . The formation of higher-order oxides through sequential addition of O_2 to titanium monoxide ion was observed in a recent study of the gas-phase reactions of transition-metal ions with molecular oxygen.²³ The same workers have also shown that VO^+ sequentially forms VO_3^+ , VO_5^+ , and VO_7^+ in the presence of oxygen under selected-ion flow tube conditions, and have provided a detailed theoretical examination of the energies and possible structures of these oxides.²⁴ We propose that the production of TiO_3^+ ions is due to the effective insertion capability of Ti^+ ion into H_2O molecules, as reflected by the large exothermicity of this reaction.

Figure 2 displays a typical TOF mass spectrum of the products of reaction between Ti^+ and dimethyl ether clusters. The spectrum was obtained using a laser pulse energy of 30 mJ/cm^2 and an argon stagnation pressure of 1.5 atm. Dimethyl ether (DME), CH_3OCH_3 , can be looked upon as an H_2O molecule in which the two H atoms are substituted by CH_3 . The spectrum in the low mass region consists of methoxy-

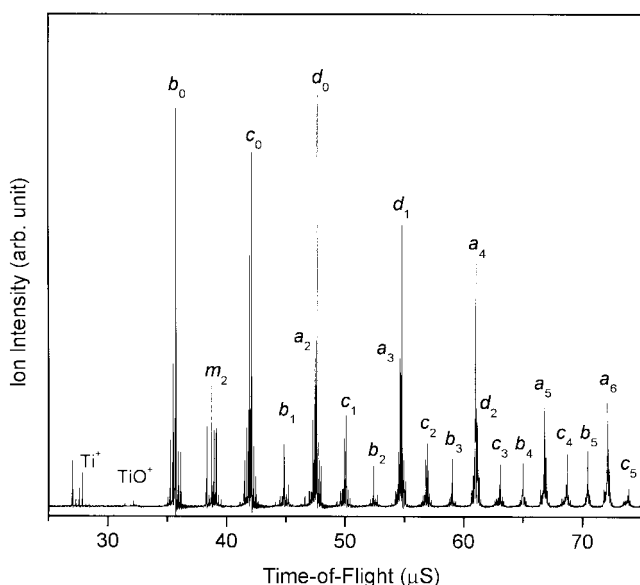
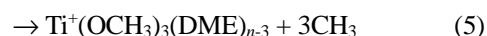
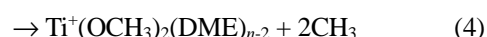


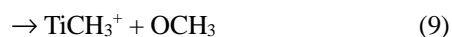
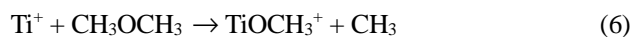
Figure 2. Time-of-flight mass spectrum showing the product ions from the reactions of Ti^+ with dimethyl ether (CH_3OCH_3) clusters. a_n : $\text{Ti}^+(\text{DME})_n$; b_n : $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$; c_n : $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$; d_n : $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$; m_n : $(\text{DME})_n\text{H}^+$. DME denotes CH_3OCH_3 .

rich fragment ions such as $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$ (b_n series), $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$ (c_n series), and $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$ (d_n series), in which the OCH_3 group is thought to be covalently bonded to the titanium ion. The prevalence of methoxy-rich fragment ions in the mass spectrum indicates that CH_3 elimination is the preferred decomposition pathway in the reaction of Ti^+ ion with CH_3OCH_3 molecules. We speculate that these heterocluster ions form as a result of $\text{Ti}^+(\text{DME})_n$ ions being consumed by sequential intracluster ion-molecule reactions:



Within the cluster, Ti^+ first inserts into the C-O bond to form $[\text{CH}_3\text{-Ti}^+\text{-OCH}_3]$ after which Ti^+OCH_3 is formed *via* CH_3 elimination. Further reactions of Ti^+OCH_3 with solvated CH_3OCH_3 molecules give rise to $\text{Ti}^+(\text{OCH}_3)_2$ and $\text{Ti}^+(\text{OCH}_3)_3$. A surprising implication of this series of cluster reactions is that CH_3 elimination in CH_3OCH_3 by the Ti^+ ion is possible for up to three dimethyl ether molecules.

Univalent gaseous metal ions react with simple ethers by an oxidative addition mechanism. Freiser *et al.*²⁵ have reported that Fe^+ reacts with dimethyl ether to produce $\text{Fe}(\text{CH}_2\text{O})^+$ and CH_4 through a mechanism involving metal insertion into the polar C-O bond followed by a β -hydride shift from the alkoxy ligand. Similarly, ion-molecule reactions of Ti^+ with CH_3OCH_3 *via* C-O bond insertion can be represented by the following reactions:



The observation of TiOCH_3^+ , TiOCH_2^+ , and TiO^+ ions in the mass spectrum indicates that these reaction pathways are energetically favorable. Other product ions such as $\text{Ti}^+\text{-CH}_3\text{OCH}_2$ and TiH^+ that result from C-H bond insertion are not observed, suggesting that the insertion of Ti^+ into the C-O bond prevails over insertion into the C-H bond of CH_3OCH_3 . The reason for this preference is addressed in detail later in this paper.

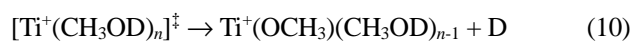
Another interesting feature of the mass spectrum shown in Figure 2 is that the chemical reactivity of the Ti^+ ion within the heterocluster is greatly influenced by the cluster size. The intensities of the $\text{Ti}^+(\text{DME})_n$ cluster ions are much lower than those of the $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_{n-2}$ cluster ions, and this trend is maintained for all clusters with $n \leq 3$. As the cluster size increases, however, the peaks corresponding to $\text{Ti}^+(\text{DME})_n$ cluster ions become dominant. This phenomenon, known as product switching, was observed in a study of the reactions $\text{Mg}^+ + (\text{H}_2\text{O})_n$ by Misaizu and co-workers.²⁶ They found that for $n < 15$ the dominant species is $\text{Mg}^+(\text{OH})(\text{H}_2\text{O})_{n-1}$, whereas for $n \geq 15$ the intact cluster ion $\text{Mg}^+(\text{H}_2\text{O})_n$ is the dominant

species and only very small quantities of $\text{Mg}^+(\text{OH})(\text{H}_2\text{O})_{n-1}$ are present. Consistent with the observations for Mg^+ clusters, the results presented here show that the reactivity of the Ti^+ ion diminishes with increasing solvation by dimethyl ether molecules. This apparent quenching of CH_3 elimination reactions is attributed to an increase in the stabilization of $\text{Ti}^+(\text{DME})_n$ cluster ions as the degree of solvation increases. Another possibility is that the dimethyl ether molecules surrounding the metal ion create an energy barrier in the reaction pathway for CH_3 elimination. Because the capability of CH_3 radical transport after C-O bond cleavage is greatly reduced within the tightly packed solvent cage of $\text{Ti}^+(\text{DME})_n$ cluster ions, the trapping probability of CH_3 radical eliminated from CH_3OCH_3 is expected to increase with cluster size.²⁷ Such an increase in trapping probability would be expected to suppress CH_3 elimination reactions in sufficiently large clusters.

The substitution of one H atom in H_2O by the more bulky CH_3 group is expected to alter the reaction pathways because the resulting molecule, CH_3OH , contains C-H, C-O, and O-H bonds. Thus, studying the $\text{Ti}^+ + \text{CH}_3\text{OH}$ system offers an opportunity to simultaneously investigate the chemical reactivity of Ti^+ toward the insertion reactions of three different chemical bonds. In addition, isotope substitution experiment using deuterated methanol, CH_3OD , enables us to determine if the peaks appearing at multiple mass units lighter than the parent ion correspond to the loss of multiple H atoms from the CH_3 group or to sequential eliminations of D from OD groups within the heteroclusters. The mass spectrum obtained from the reactions of Ti^+ with $(\text{CH}_3\text{OD})_n$ obtained with a laser pulse energy of 15 mJ/cm^2 and an argon stagnation pressure of 1 atm is presented in Figure 3. The mass spectrum exhibits a sequence of $(\text{CH}_3\text{OD})_n\text{D}^+$ cluster ions (m_n), which

can be attributed to protonated clusters formed by the protonation of the generated parent cluster ions. In the high mass region of the spectrum, the dominant cluster ions consist of a series of heterocluster ions of $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OD})_n$ ($m = 1-3$) produced by intracluster ion-molecule reactions. With isotopically unsubstituted methanol, mass spectral measurements cannot distinguish between methoxide ($-\text{OCH}_3$) and hydroxymethyl ($-\text{CH}_2\text{OH}$) products, the former resulting from O-H cleavage, the latter from C-H cleavage. The mass spectrum clearly shows distinct peaks separated by 2 amu spacings corresponding to $\text{Ti}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_{n-1}$, $\text{Ti}^+(\text{OCH}_3)_2(\text{CH}_3\text{OD})_{n-2}$, and $\text{Ti}^+(\text{OCH}_3)_3(\text{CH}_3\text{OD})_{n-3}$, which can only arise from successive O-D bond cleavages in the association complex $\text{Ti}^+(\text{CH}_3\text{OD})_n$. This result is in good agreement with the data of Lu and Yang,²⁷ who claim that the hydrogen atom elimination channel of Mg^+ with methanol clusters leads to product ions with apparent stoichiometry $\text{MgOCH}_3^+(\text{CH}_3\text{OH})_n$.

Similar to the reactions of Ti^+ with CH_3OCH_3 , these ions can be interpreted as resulting from sequential D elimination reactions:



These D elimination reactions occur for up to three methanol molecules, which is similar to the behavior observed for the $\text{Ti}^+ + \text{CH}_3\text{OCH}_3$ system. Ti^+ insertion into the C-H, C-O, and O-D bonds of a methanol molecule leads to three intermediates: $[\text{H-Ti}^+-\text{CH}_2\text{OD}]$, $[\text{DO-Ti}^+-\text{CH}_3]$, and $[\text{D-Ti}^+-\text{OCH}_3]$. Given that Ti^+-OCH_3 is the dominant ionic product observed in the present experiments, it is therefore clear that the insertion of Ti^+ into the O-D bond to form the intermediate $[\text{D-Ti}^+-\text{OCH}_3]$ is the most favorable of the three possible reaction channels.

The observation of a mass peaks corresponding to the TiO^+ and TiOD^+ ions is primarily attributable to the elimination of CH_3D and CH_3 from the $[\text{DO-Ti}^+-\text{CH}_3]$ intermediate formed by Ti^+ insertion into the 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^+ ,²⁸ Fe^+ ,²⁹ and Sr^+ ,³⁰ and has been found to coincide with the elimination of CH_3 . Since the $\text{CH}_3\text{-OH}$ bond energy is 92.4 kcal/mol ¹⁹ and the binding energy of Ti^+-OH is 111.1 kcal/mol ,³¹ we estimate that the ground-state reaction for $\text{Ti}^+ + \text{CH}_3\text{OH} \rightarrow \text{Ti}^+-\text{OH} + \text{CH}_3$ 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.³² Further analysis of the mass spectrum reveals that other reaction products corresponding to $\text{TiO}^+(\text{CH}_3\text{OD})_n$ and $\text{TiO}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_n$ ions (denoted p_n and q_n respectively) also appear but with much smaller intensities. The observation of these ions indicates that TiO^+ formed from the ion-molecule reaction $\text{Ti}^+ + \text{CH}_3\text{OD}$ can undergo subsequent D-elimination reactions with methanol within the

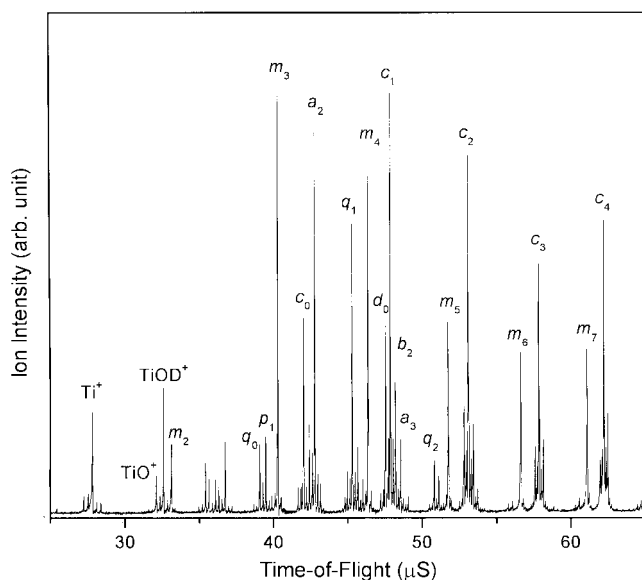


Figure 3. Time-of-flight mass spectrum showing the product ions from the reactions of Ti^+ with CH_3OD seeded in 1 atm Ar. The laser fluence is 15 mJ/cm^2 . a_n : $\text{Ti}^+(\text{CH}_3\text{OD})_n$; b_n : $\text{Ti}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_n$; c_n : $\text{Ti}^+(\text{OCH}_3)_2(\text{CH}_3\text{OD})_n$; d_n : $\text{Ti}^+(\text{OCH}_3)_3(\text{CH}_3\text{OD})_n$; p_n : $\text{TiO}^+(\text{CH}_3\text{OD})_n$; q_n : $\text{TiO}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_n$; m_n : $(\text{CH}_3\text{OD})_n\text{D}^+$.

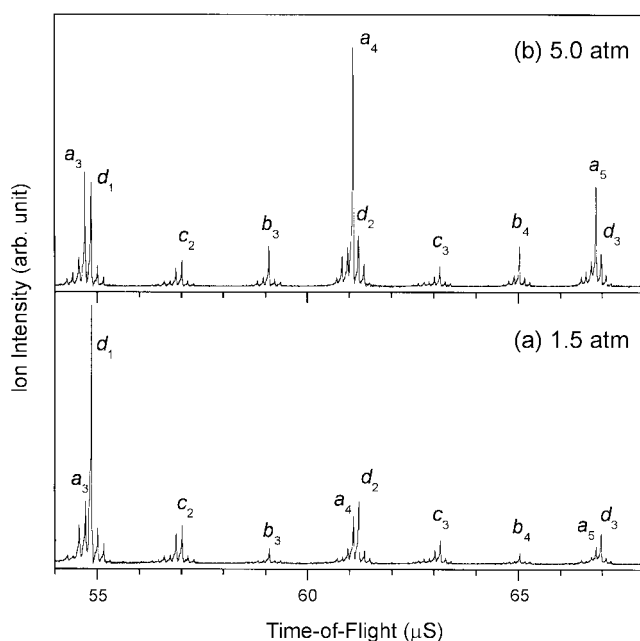


Figure 4. Time-of-flight mass spectra resulting from the reactions of Ti^+ with CH_3OCH_3 clusters at Ar stagnation pressures of (a) 1.5 atm and (b) 5.0 atm. a_n : $\text{Ti}^+(\text{DME})_n$; b_n : $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$; c_n : $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$; d_n : $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$. DME denotes CH_3OCH_3 .

clusters.

To investigate the solvent effect of argon atoms on the abundance distribution of heterocluster ions, the mass spectrum was measured at two different stagnation pressures. Figure 4 shows the mass spectra obtained when dimethyl ether is seeded in 1.5 and 5 atm argon. Each spectrum covers the same mass range, which has been chosen to show peaks corresponding to $\text{Ti}^+(\text{OCH}_3)_m(\text{DME})_n$ clusters ($3 \leq m + n \leq 6$). When CH_3OCH_3 vapor seeded in 1.5 atm argon is expanded, the CH_3 , 2CH_3 , and 3CH_3 elimination products corresponding to $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$ (b_n series), $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$ (c_n series), and $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$ (d_n series) are observed, with the 3CH_3 elimination process dominating. This implies that the intracluster ion-molecule reactions of Ti^+ with dimethyl ether clusters readily occur in these clusters. As the argon stagnation pressure is increased, however, the solvation of Ti^+ ions by neutral CH_3OCH_3 molecules becomes unfavorable due to the lower fraction of dimethyl ether in the gas mixture. Expansion of dimethyl ether vapor at 5 atm gives rise to a very distinctive feature in the mass spectrum (Figure 4b). At higher Ar pressure the abundance of $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$ ions substantially decreases, in contrast to the behavior at low Ar stagnation pressure, where $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_n$ ions are highly abundant in comparison with the $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$ and $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$ species. 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 dimethyl ether molecules in the heterocluster and the reaction probability of the Ti^+ ion with dimethyl ether is greatly suppressed by the argon moieties. The effective cooling of heterocluster ions formed from the

Table 1. Energetics of Possible Reaction Pathways of Ti^+ with H_2O , CH_3OCH_3 , and CH_3OH^a

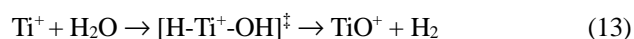
Reactant	Insertion Site	Reaction Products	Enthalpy (kcal/mol)	
H_2O	O-H Bond \rightarrow	$\text{TiO}^+ + \text{H}_2$	-42.5	
		$\text{TiOH}^+ + \text{H}$	8.2	
		$\text{TiH}^+ + \text{OH}$	65.1	
CH_3OCH_3	C-O Bond \rightarrow	$\text{TiO}^+ + \text{C}_2\text{H}_6$	-76.4	
		$\text{TiOCH}_3^+ + \text{CH}_3$	-28.3 ^b	
		$\text{TiCH}_3^+ + \text{OCH}_3$	25.5	
CH_3OD	C-H Bond \rightarrow	$\text{Ti}^+\text{CH}_3\text{OCH}_2 + \text{H}$	38.7	
		$\text{TiH}^+ + \text{CH}_3\text{OCH}_2$	42.0	
		C-O Bond \rightarrow	$\text{TiO}^+ + \text{CH}_3\text{D}$	-68.8
CH_3OD	O-D Bond \rightarrow	$\text{TiOD}^+ + \text{CH}_3$	-18.7	
		C-H Bond \rightarrow	$\text{TiOCH}_3^+ + \text{D}$	-6.9
		C-H Bond \rightarrow	$\text{Ti}^+\text{CH}_2\text{OD} + \text{H}$	36.4 ^c
		$\text{TiH}^+ + \text{CH}_2\text{OD}$	39.7	

^aReaction enthalpies are calculated from the thermochemical data provided in Refs. 19, 33, and 34. ^bThe bond energy $D_0(\text{Ti}^+-\text{OCH}_3)$ is assumed to be equal to $D_0(\text{Ti}^+-\text{OH})$. ^cThe bond energy $D_0(\text{Ti}^+-\text{CH}_2\text{OD})$ is assumed to be equal to $D_0(\text{Ti}^+-\text{CH}_3)$.

supersonic jet at high stagnation pressure would also contribute to the decreased chemical reactivity. The present results suggest that CH_3 elimination reactions are highly dependent on the argon concentration within the clusters, which is consistent with our previous studies of the reactions of Ti^+ with CH_3OH clusters.¹⁸

Discussion

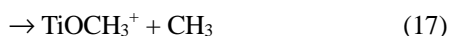
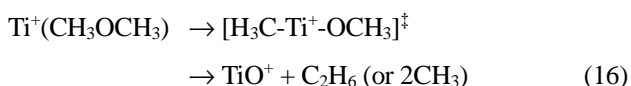
Water molecules contain only one type of O-H chemical bond that might permit the insertion of a Ti^+ ion. Thus, ion-molecule reactions within $\text{Ti}^+(\text{H}_2\text{O})_n$ clusters appear to have three possible elimination channels.



The enthalpies of these ion-molecule reactions, estimated from thermochemical data,^{19,33,34} are listed in Table 1. Formation of $\text{TiOH}^+ + \text{H}$ or $\text{TiH}^+ + \text{OH}$ can occur from the $[\text{H-Ti}^+-\text{OH}]$ intermediate by simple Ti^+-H or Ti^+-OH bond fission, respectively. The complete absence of TiOH^+ and TiH^+ ions in the present mass spectrum strongly suggests that reactions 14 and 15 are energetically unfavorable due to their endothermic enthalpy changes of 8.2 and 65.1 kcal/mol. The dominant TiO^+ formation channel can proceed from the $[\text{H-Ti}^+-\text{OH}]$ intermediate through a four-centered transition state, as suggested by Armentrout and co-workers.¹² This reaction channel is exothermic, with enthalpy change of -42.5 kcal/mol. As an alternative mechanism, $\text{TiO}^+ + \text{H}_2$ products can also be produced via the formation of an $[\text{H}_2\text{Ti}^+-\text{O}]$ transition state followed by elimination of H_2 .³³ We note that because Ti^+ has three valence electrons it can form an $[\text{H}_2\text{Ti}^+-\text{O}]$ intermediate. In our experiments, we

have no direct method for determining which process occurs after the formation of $[\text{H-Ti}^+-\text{OH}]$; further work will be needed to fully understand these reactions.

The dimethyl ether molecule possesses two types of chemical bonds, C-O and C-H. If Ti^+ inserts into the C-H bond to form the intermediate $[\text{H-Ti}^+-\text{CH}_2\text{OCH}_3]$, the product ions TiH^+ or $\text{Ti}^+\text{CH}_2\text{OCH}_3$ are expected to form through Ti^+-C or Ti^+-H bond dissociations, respectively. However, these product ions are not observed in the mass spectrum, indicating that the C-H insertion process does not occur within the heteroclusters. This result is consistent with the high endothermicity of the C-H insertion reaction (42.0 kcal/mol and 38.7 kcal/mol for the Ti^+-H and $\text{Ti}^+-\text{CH}_2\text{OCH}_3$ formation channels, respectively). The thermodynamic data also show that the $\text{H}_3\text{C-OCH}_3$ bond dissociation energy is 83.3 kcal/mol,³⁴ which is less than that of the $\text{H-CH}_2\text{OCH}_3$ bond (ca. 94 kcal/mol). Thus, insertion of Ti^+ ion into C-O bond seems more energetically favorable than insertion into C-H bond. The C-O insertion reaction of the Ti^+ ion produces TiO^+ and TiOCH_3^+ ions, which are in fact observed in the present experiments. These reactions within the heterocluster ions are summarized as follows.

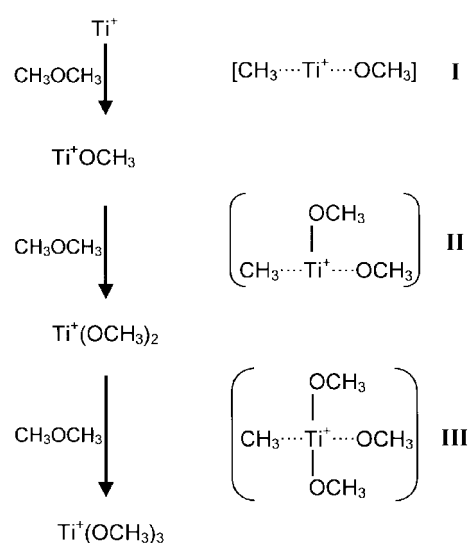


The enthalpy changes of reactions 16 and 17 show exothermicities of -76.4 and -28.3 kcal/mol respectively, suggesting that these reactions will occur as they become energetically feasible.

Similar to the mechanism of the $\text{Ti}^+ + \text{H}_2\text{O} \rightarrow \text{TiO}^+ + \text{H}_2$ reaction, the TiO^+ formation channel can proceed from the $[\text{H}_3\text{C-Ti}^+-\text{OCH}_3]$ intermediate through a four-centered transition state. The TiO^+ ion can also be produced from the intermediate by β -methyl radical transfer to the metal ion, forming C_2H_6 , which is then lost as a neutral product. However, the fact that only minor contributions from TiO^+ ions are evident in the mass spectra demonstrates that the C_2H_6 elimination pathways (either *via* a four-centered transition state or CH_3 migration) are less efficient routes than the CH_3 elimination channel (reaction 17) for producing $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OCH}_3)_n$ ions, even though the former process is more exothermic than the latter. The predominant formation of TiOCH_3^+ from the $[\text{H}_3\text{C-Ti}^+-\text{OCH}_3]$ intermediate is also plausible, because the energy required for the bond dissociation D_0^0 of Ti^+-CH_3 (57.5 kcal/mol)³⁵ is much lower than that of Ti^+-OCH_3 (111 kcal/mol) assuming D_0^0 (Ti^+-OCH_3) is equal to D_0^0 (Ti^+-OH).³¹

One surprising finding of the present work is that $\text{Ti}^+(\text{OCH}_3)(\text{CH}_3\text{OCH}_3)_n$ cluster ions can react further to give $\text{Ti}^+(\text{OCH}_3)_3(\text{CH}_3\text{OCH}_3)_n$. In Scheme 1 we propose a mechanism for the consecutive intracuster reactions of Ti^+ with the dimethyl ether moiety.

Within the stabilizing environs of a heterocluster, the reaction is initiated by Ti^+ insertion into a C-O bond of one



Scheme 1

of the solvating dimethyl ether molecules to form the intermediate **I**. This intermediate then dissociates internally and $\text{Ti}^+(\text{OCH}_3)$ ion is produced *via* CH_3 elimination, with the OCH_3 group behaving more like a tightly bound group than a solvating ligand species. No experimental data for the bond energies of transition metal ion-ether complexes are reported in the literature. This paucity of data may be due to the fact that transition metal ions readily insert into the C-O bond of ethers,³⁶⁻³⁸ which makes it difficult to determine whether the bond energy being determined is that of an insertion complex or an association complex. The binding energy of Mg^+-OCH_3 (67.35 kcal/mol)²⁷ is known to be much stronger than that of $\text{Mg}^+-\text{CH}_3\text{OCH}_3$ (38.3 kcal/mol);³⁹ thus, the bonding in the Ti^+OCH_3 ion is likely to resemble covalent rather than electrostatic binding. Similarly, insertion of the Ti^+OCH_3 ion into a second dimethyl ether molecule, followed by CH_3 elimination, results in the formation of $\text{Ti}^+(\text{OCH}_3)_2$. Around the $\text{Ti}^+(\text{OCH}_3)_2$ ion, there is room for one additional dimethyl ether molecule, forming intermediate **III**. The complete absence of cluster ions with formula $\text{Ti}^+(\text{OCH}_3)_4(\text{CH}_3\text{OCH}_3)_n$ in the mass spectrum suggests that the coordination of three OCH_3 groups around a Ti^+ ion greatly reduces the ability of Ti^+ to break the C-O bond of additional dimethyl ether 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 tetravalent structures commonly observed for neutral titanium compounds such as TiCl_4 and $\text{Ti}(\text{OR})_4$, where $\text{R} = \text{CH}_3$, isopropyl, and *tert*-butyl.

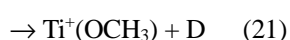
We now consider the reactions of the Ti^+ ion with methanol clusters. The intracuster reaction of $\text{Ti}^+(\text{CH}_3\text{OD})_n$ appears to have three elimination channels open, D, CH_3 , and CH_3D elimination, with D-elimination predominating. There are three types of chemical bonds in a methanol molecule that might permit the insertion of a Ti^+ ion: C-H, C-O, and O-D. Insertion into the C-H bond does not occur within the methanol heteroclusters, as has also been confirmed for the

reaction of Ti^+ with dimethyl ether clusters. The C-O insertion reactions of the Ti^+ ion within the heterocluster ions are



Reactions 18 and 19 are exothermic, with enthalpy changes of -68.8 and -18.7 kcal/mol, respectively. These enthalpy changes are consistent with the clear observation of TiOD^+ and TiO^+ in the mass spectrum.

We suggest that a major reaction channel of $\text{Ti}^+(\text{CH}_3\text{OD})_n$ is the insertion of the Ti^+ ion into the O-D bond of one of the solvating methanol molecules:



The formation of the TiD^+ ion *via* Ti^+-OCH_3 bond rupture is unfavorable due to the relatively low dissociation energy (53.9 kcal/mol)⁴⁰ of the Ti-D bond. TiO^+ formation from reaction 20 is similar to that from reaction 18, as mentioned above. The present mass spectral data alone are insufficient to unequivocally assign the formation mechanism of TiO^+ to reaction 18 or 20. The lower intensity of the TiO^+ ion peak in the mass spectrum in comparison to those of D elimination products such as $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OD})_n$ clusters implies that the TiO^+ ion is not produced from an O-D insertion reaction. Thus, we suggest that reaction 18 prevails over reaction 20.

Simple consideration of the strengths of the bonds in the CH_3OH molecule predicts that C-H collisional activation is both energetically and statistically favored over activation of the O-H bond. The thermodynamic data show that the C-H and C-O bond dissociation energies are 93.9 and 92.4 kcal/mol, respectively, which are less than that of the O-H bond (104.2 kcal/mol).⁴¹ Likewise, C-H and C-O bond dissociation reactions seem more energetically facile than the O-D insertion reaction in the case of CH_3OD . Despite the large O-D bond dissociation energy, however, it is this D elimination that is observed to predominate in the present experiments. One possible rationale for this is that the breakage of the O-D bond in CH_3OD is compensated for by the formation of a Ti^+-OCH_3 bond. The binding energy of Ti^+-OCH_3 is not available. However, considering that CH_3 is more polarizable than H and that this polarizability would increase the ligand contribution to the bonding,⁴² we expect the binding energy of Ti^+-OCH_3 to be larger than that of Ti^+-OH (111 kcal/mol). Thus, although the bond dissociation energy of $\text{CH}_3\text{O-D}$ is 11.8 kcal/mol larger than that of $\text{CH}_3\text{-OD}$, the large bond dissociation energy of Ti^+-OCH_3 may still make the D-elimination reaction exothermic.

Conclusion

The reactions that proceed within $\text{Ti}^+(\text{H}_2\text{O})_n$, $\text{Ti}^+(\text{CH}_3\text{OCH}_3)_n$, and $\text{Ti}^+(\text{CH}_3\text{OD})_n$ heterocluster ions were studied using the laser vaporization-molecular beam method. In the reactions of Ti^+ with water clusters, the formation of $\text{TiO}^+ + \text{H}_2$ is the

dominant process. The primary reactions of Ti^+ ions with CH_3OCH_3 clusters produce a major sequence of cluster ions with the formula $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OCH}_3)_n$, which is attributed to the oxidative insertion of Ti^+ ion into the C-O bond of dimethyl ether followed by CH_3 elimination. Insertions of Ti^+ ions into the O-D bonds of methanol molecules within the heteroclusters play an important role in producing $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OD})_n$ ions. These insertion reactions by the Ti^+ ion were found to occur for up to three precursor molecules. The formation of TiO^+ ion is interpreted as arising from the insertion of Ti^+ ions into the O-H bond of H_2O or C-O bond of CH_3OCH_3 and CH_3OD , followed by molecular elimination from the $[\text{R-Ti}^+-\text{OR}]$ intermediate (R = H or CH_3). From these observations, we conclude that the chemical reactivity of Ti^+ ion toward the three different chemical bonds in methanol is in the order O-H > C-O > C-H. The chemical reactivity of Ti^+ ions within the heteroclusters decreases with increasing cluster size and increasing argon stagnation pressure.

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