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

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The intracluster ion-molecule reactions of Ti$^+$(H$_2$O)$_n$, Ti$^+$(CH$_3$OCH$_3$)$_n$, and Ti$^+$(CH$_3$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 TiO$^+$(H$_2$O)$_n$ clusters. The mass spectra resulting from the reactions of Ti$^+$ with CH$_3$OCH$_3$ clusters exhibit a major sequence of Ti$^+$(OCH$_3$)$_m$(CH$_3$OCH$_3$)$_n$ cluster ions, which is attributed to the insertion of Ti$^+$ ion into C-O bond of CH$_3$OCH$_3$ followed by CH$_3$ elimination. The prevalence of Ti$^+$(OCH$_3$)$_m$(CH$_3$OCH$_3$)$_n$ ions in the reaction of Ti$^+$ with CH$_3$OD 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.$^2$ 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.$^{9,10}$ In studies of the reaction of Ti$^+$ with water using selected ion drift tube technique$^{11}$ 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$^+$. 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$_2$O, CH$_3$OCH$_3$, and CH$_3$OD 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 CH₃ 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. 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 ≤ 1 mm². The laser fluence at the target surface was varied in the range 10-100 mJ/cm². 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 heterocluster ions of formula TiO⁺ (H₂O)ₙ. The ion complexes to form titanium oxide clusters. The intact cluster ions Ti⁺(H₂O)ₙ, stem from the association reaction between Ti⁺ and water clusters, possibly followed by evaporation of water molecules:

\[
\text{Ti⁺ + (H₂O)ₙ \rightarrow [Ti⁺(H₂O)ₙ]⁺ \rightarrow Ti⁺(H₂O)ₙ + (m-n)H₂O (1)}
\]

The evaporation of H₂O 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.

The dehydrogenation reaction within a Ti⁺(H₂O)ₙ, cluster ion can be expressed as follows:

\[
[\text{Ti⁺(H₂O)ₙ}]⁺ \rightarrow \text{TiO⁺(H₂O)ₙ₋₁} + \text{H₂ (2)}
\]

A reaction of this type has been recently observed in a gas phase ion-molecule reaction of Ti⁺ with H₂O at thermal energies. The formation of TiO⁺ is not surprising given the fact that Ti⁺ forms very strong bonds with oxygen atoms. One might speculate that the TiO⁺ ions arise from the Ti target. Prior to the seeding of the H₂O vapor, pure Ar gas was

![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/cm². a₁: Ti⁺(H₂O)ₚ, p: TiO⁺(H₂O)ₚ, x: TiO⁺(H₂O)₁; w: (H₂O)⁺. Peaks corresponding to the natural abundances of the isotopes of titanium (⁴⁶Ti, 8.0%; ⁴⁷Ti, 7.3%; ⁴⁸Ti, 73.8%; ⁴⁹Ti, 5.5%; ⁵⁰Ti, 5.4%).]
Cluster Reactions of Titanium Heteroclusters


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⁺ 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 TiO⁺(H₂O)ₙ (labeled sₙ) is particularly intriguing. This implies that TiO⁺ ion produced in reaction 2 reacts further in sequential dehydrogenation reactions with H₂O molecules to form TiO₂⁺. The formation of higher-order oxides through sequential addition of O₂ to titanium monoxide ion was observed in a recent study of the gas-phase reactions of transition-metal ions with molecular oxygen. The same workers have also shown that VO⁺ sequentially forms VO₂⁺, VO₃⁺, and VO₅⁺ 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. We propose that the production of TiO₂⁺ ions is due to the effective insertion capability of Ti⁺ ion into H₂O 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/cm² and an argon stagnation pressure of 1.5 atm. Dimethyl ether (DME), CH₃OCH₃, can be looked upon as an H₂O molecule in which the two H atoms are substituted by CH₃. The spectrum in the low mass region consists of methoxy-rich fragment ions such as Ti⁺(OCH₃)(DME)ₙ (bₙ series), Ti⁺(OCH₂)(DME)ₙ (cₙ series), and Ti⁺(OCH₃)₂(DME)ₙ (dₙ series), in which the OCH₃ group is thought to be covalently bonded to the titanium ion. The prevalence of methoxy-rich fragment ions in the mass spectrum indicates that CH₃ elimination is the preferred decomposition pathway in the reaction of Ti⁺ ion with CH₃OCH₃ molecules. We speculate that these heterocluster ions form as a result of Ti⁺(DME)ₙ ions being consumed by sequential intracluster ion-molecule reactions:

\[ \text{Ti⁺(DME)ₙ} \rightarrow \text{Ti⁺(OCH₃)(DME)ₙ} + \text{CH₃} \]  
\[ \rightarrow \text{Ti⁺(OCH₃)₂(DME)ₙ} + 2\text{CH₃} \]  
\[ \rightarrow \text{Ti⁺(OCH₃)₃(DME)ₙ} + 3\text{CH₃} \]

Within the cluster, Ti⁺ first inserts into the C-O bond to form [CH₃-Ti⁺-OCH₃] after which Ti⁺OCH₃ is formed via CH₃ elimination. Further reactions of Ti⁺OCH₃ with solvated CH₃OCH₃ molecules give rise to Ti⁺(OCH₃)₂ and Ti⁺(OCH₃)₃. A surprising implication of this series of cluster reactions is that CH₃ elimination in CH₃OCH₃ 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. have reported that Fe⁺ reacts with dimethyl ether to produce Fe(CH₂O)⁺ and CH₄ 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 CH₃OCH₃ via C-O bond insertion can be represented by the following reactions:

\[ \text{Ti⁺ + CH₃OCH₃} \rightarrow \text{TiOCH₃⁺ + CH₃} \]  
\[ \rightarrow \text{TiOCH₂⁺ + CH₄} \]  
\[ \rightarrow \text{TiO⁺ + C₂H₄} \]  
\[ \rightarrow \text{TiCH₃⁺ + OCH₃} \]

The observation of TiOCH₃⁺, TiOCH₂⁺, and TiO⁺ ions in the mass spectrum indicates that these reaction pathways are energetically favorable. Other product ions such as Ti⁺-CH₃OCH₂ 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 CH₃OCH₃. 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 Ti⁺(DME)ₙ clusters are much lower than those of the Ti⁺(OCH₃)₂(DME)ₙ cluster ions, and this trend is maintained for all clusters with \( n \leq 3 \). As the cluster size increases, however, the peaks corresponding to Ti⁺(DME)ₙ cluster ions become dominant. This phenomenon, known as product switching, was observed in a study of the reactions Mg⁺ + (H₂O)ₙ by Misaizu and co-workers. They found that for \( n < 15 \) the dominant species is Mg⁺(OH)(H₂O)ₙ⁻, whereas for \( n \geq 15 \) the intact cluster ion Mg⁺(H₂O)ₙ is the dominant product.
species and only very small quantities of Mg\textsuperscript{+}(OH)(H\textsubscript{2}O)\textsubscript{n},\textsubscript{1} are present. Consistent with the observations for Mg\textsuperscript{+} clusters, the results presented here show that the reactivity of the Ti\textsuperscript{+} ion diminishes with increasing solvation by dimethyl ether molecules. This apparent quenching of CH\textsubscript{3} elimination reactions is attributed to an increase in the stabilization of Ti\textsuperscript{+}(DME)\textsubscript{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\textsubscript{3} elimination. Because the capability of CH\textsubscript{3} radical transport after C-O bond cleavage is greatly reduced within the tightly packed solvent cage of Ti\textsuperscript{+}(DME)\textsubscript{n} cluster ions, the trapping probability of CH\textsubscript{3} radical eliminated from CH\textsubscript{3}OCH\textsubscript{3} is expected to increase with cluster size\textsuperscript{27}. Such an increase in trapping probability would be expected to suppress CH\textsubscript{3} elimination reactions in sufficiently large clusters.

The substitution of one H atom in H\textsubscript{2}O by the more bulky CH\textsubscript{3} group is expected to alter the reaction pathways because the resulting molecule, CH\textsubscript{3}OH, contains C-H, C-O, and O-H bonds. Thus, studying the Ti\textsuperscript{+} + CH\textsubscript{3}OH system offers an opportunity to simultaneously investigate the chemical reactivity of Ti\textsuperscript{+} toward the insertion reactions of three different chemical bonds. In addition, isotope substitution experiment using deuterated methanol, CH\textsubscript{3}OD, 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\textsubscript{3} group or to sequential eliminations of D from OD molecules, which is similar to the behavior observed for the reactions of alkaline earth metal ions with methanol, including Mg\textsuperscript{+},\textsuperscript{28} Fe\textsuperscript{+},\textsuperscript{29} and Sr\textsuperscript{+},\textsuperscript{30} and has been found to coexist with the elimination of CH\textsubscript{3}D and CH\textsubscript{3}. From the data of Lu and Yang,\textsuperscript{27} who claim that the hydrogen atom elimination channel of Mg\textsuperscript{+} with methanol clusters leads to product ions with apparent stoichiometry MgOCH\textsubscript{3}+(CH\textsubscript{3}OH)\textsubscript{n}, the observation of these ions indicates that TiO\textsuperscript{+} formed from CH\textsubscript{3}OH molecule. The formation of metal hydroxide ions from methanol has been observed in other metal ion systems, including Mg\textsuperscript{+},\textsuperscript{28} Fe\textsuperscript{+},\textsuperscript{29} and Sr\textsuperscript{+},\textsuperscript{30} and has been found to coincide with the elimination of CH\textsubscript{3}. Since the CH\textsubscript{3}OH bond energy is 92.4 kcal/mol,\textsuperscript{31} we estimate that the ground-state bond energy of Ti\textsuperscript{+}-OH is 111.1 kcal/mol,\textsuperscript{32} and the binding energy of Ti\textsuperscript{+} + CH\textsubscript{3}OH → Ti\textsuperscript{+}-OH + CH\textsubscript{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.\textsuperscript{32} Further analysis of the mass spectrum reveals that other reaction products corresponding to TiO\textsuperscript{+}(CH\textsubscript{3}OD)\textsubscript{n} and TiO\textsuperscript{+}(OCH\textsubscript{3})(CH\textsubscript{3}OD)\textsubscript{n} ions (denoted \(p_n\) and \(q_n\), respectively) also appear but with much smaller intensities. The observation of these ions indicates that TiO\textsuperscript{+} formed from the ion-molecule reaction Ti\textsuperscript{+} + CH\textsubscript{3}OD can undergo subsequent D-elimination reactions with methanol within the

\[
\begin{align*}
\text{Ti}^+ (\text{CH}_3OD)_n &\rightarrow \text{Ti}^+ (\text{OCH}_3)(\text{CH}_3OD)_{n-1} + \text{D} \ (11) \\
&\rightarrow \text{Ti}^+ (\text{OCH}_3)(\text{CH}_3OD)_{n-2} + 2\text{D} \ (12) \\
&\rightarrow \text{Ti}^+ (\text{OCH}_3)(\text{CH}_3OD)_{n-3} + 3\text{D} \ (12)
\end{align*}
\]
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 two different mass ranges, which have been chosen to show peaks corresponding to Ti+(OCH₃)ₙ(DME)ₙ clusters (3 ≤ m + n ≤ 6). When CH₃OCH₃ vapor seeded in 1.5 atm argon is expanded, the CH₃, 2CH₃, and 3CH₃ elimination products from the CH₃OCH₃ molecule reactions within Ti+(H₂O)ₙ clusters (3 ≤ m + n ≤ 6) are observed, with the 3CH₃ 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 CH₃OCH₃ 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 Ti+(OCH₃)ₙ(DME)ₙ ions substantially decreases, in contrast to the behavior at low Ar stagnation pressure, where Ti+(OCH₃)ₙ(DME)ₙ ions are highly abundant in comparison with the Ti+(OCH₃)ₙ(DME)ₙ and Ti+(OCH₃)₂(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 supersonic jet at high stagnation pressure would also contribute to the decreased chemical reactivity. The present results suggest that CH₃ 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 CH₃OH clusters.

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 Ti⁺(H₂O)ₙ clusters appear to have three possible elimination channels.

\[
\begin{align*}
\text{Ti⁺} + \text{H₂O} & \rightarrow [\text{H-Ti⁺-OH}]^+ \rightarrow \text{TiO⁺} + \text{H}_2 & \text{(13)} \\
& \rightarrow \text{TiOH⁺} + \text{H} & \text{(14)} \\
& \rightarrow \text{TiH⁺} + \text{OH} & \text{(15)}
\end{align*}
\]

Table 1. Energetics of Possible Reaction Pathways of Ti⁺ with H₂O, CH₃OCH₃, and CH₃OH

<table>
<thead>
<tr>
<th>Reactant Insertion Site</th>
<th>Reaction Products</th>
<th>Enthalpy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>O-H Bond →</td>
<td>TiO⁺ + H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiOH⁺ + H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiH⁺ + OH</td>
</tr>
<tr>
<td>CH₃OCH₃</td>
<td>C-O Bond →</td>
<td>TiO⁺ + CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiOCH₃⁺ + CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiCH₃⁺ + OCH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti⁺ + CH₃OCH₂ + H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiH⁺ + CH₃OCH₂</td>
</tr>
<tr>
<td>CH₃OD</td>
<td>C-O Bond →</td>
<td>TiO⁺ + CH₃D</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiOD⁺ + CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiOH⁺ + CH₃OD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti⁺ + CH₃OD + H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiH⁺ + CH₃OD</td>
</tr>
</tbody>
</table>

*Reaction enthalpies are calculated from the thermochemical data provided in Refs. 19, 33, and 34. The bond energy Dₑ(Ti⁺-OCH₃) is assumed to be equal to Dₑ(Ti⁺-OH). The bond energy Dₑ(Ti⁺-CH₃OD) is assumed to be equal to Dₑ(Ti⁺-CH₃).
have no direct method for determining which process occurs after the formation of [H-Ti'-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 [H-Ti'-CH3OCH3], the product ions TiH2+ or Ti(CH3)2OCH3 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 Ti'-CH3OCH3 formation channels, respectively). The thermodynamic data also show that the H3C-OCH3 bond dissociation energy is 83.3 kcal/mol,34 which is less than that of the H-CH2OCH3 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 TiOCH3+, ions, which are in fact observed in the present experiments. These reactions within the heterocluster ions are summarized as follows.

\[
\text{Ti}'(\text{CH3OCH3}) \rightarrow [\text{H}-\text{C}•\text{Ti}'•-\text{OCH3}] \rightarrow \text{TiO}^+ + \text{C}_2\text{H}_6 \text{ (or } 2\text{CH}_3) \\
\rightarrow \text{TiOCH3}^+ + \text{CH}_3 \\
\text{TiO}^+ + \text{H}_2 \rightarrow \text{TiO}^+ \text{ (OCH3) + C}_2\text{H}_6 \\
\text{TiO}^+ + \text{H}_2 \rightarrow \text{TiO}^+ \text{ (OCH3) + 2CH}_3 \\
\text{TiO}^+ + \text{H}_2 \rightarrow \text{TiO}^+ \text{ (OCH3) + C}_2\text{H}_6}
\]

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 Ti' + H2O → TiO+ + H2 reaction, the TiO+ formation channel can proceed from the [H3C-Ti'-OCH3] intermediate through a four-centered transition state. The TiO+ ion can also be produced from the intermediate by b-methyl radical transfer to the metal ion, forming C2H6, 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 C2H6 elimination pathways (either via a four-centered transition state or CH3 migration) are less efficient routes than the CH3 elimination channel (reaction 17) for producing TiO(OCH3)n(CH3OCH3)m ions, even though the former process is more exothermic than the latter. The predominant formation of TiOCH3+ from the [H3C-Ti'-OCH3] intermediate is also plausible, because the energy required for the bond dissociation D\text{F} of Ti'-CH3 (57.5 kcal/mol)\text{35} is much lower than that of Ti'-OCH3 (111 kcal/mol)\text{35} assuming D\text{F} of Ti'-OCH3 is equal to D\text{F} of Ti'-OH.\text{31}

One surprising finding of the present work is that TiO(OCH3)3(CH3OCH3) and TiO(OCH3)2(CH3OCH3) cluster ions can react further to give TiO(OCH3)3(CH3OCH3) and TiO(OCH3)2(CH3OCH3) in Scheme 1 we propose a mechanism for the consecutive intracluster 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 of the solvating dimethyl ether molecules to form the intermediate I. This intermediate then dissociates internally and Ti'('OCH3) is produced via CH3 elimination, with the OCH3 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,\text{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+-OCH3 (67.35 kcal/mol)\text{57} is known to be much stronger than that of Mg+-CH3OCH3 (38.3 kcal/mol);\text{39} thus, the bonding in the Ti'OCH3 ion is likely to resemble covalent rather than electrostatic binding. Similarly, insertion of the Ti'OCH3 ion into a second dimethyl ether molecule, followed by CH3 elimination, results in the formation of TiO('OCH3). Around the Ti'O('OCH3)2 ion, there is room for one additional dimethyl ether molecule, forming intermediate III. The complete absence of cluster ions with formula TiO('OCH3)2(CH3OCH3) in the mass spectrum suggests that the coordination of three OCH3 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 TiCl4 and Ti(OR)4, where R = CH3, isopropyl, and tert-butyl.

We now consider the reactions of the Ti' ion with methanol clusters. The intracluster reaction of Ti'(CH3OD) appears to have three elimination channels open, D, CH3, and CH3D 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

\[ \text{Ti}^+ (\text{CH}_3 \text{OD}) \rightarrow \text{[DO-Ti}^+-\text{CH}_3\text{]}^+ \rightarrow \text{TiO} + \text{CH}_3\text{D} \quad (18) \]

\[ \rightarrow \text{TiOD}^+ + \text{CH}_3 \quad (19) \]

Reactions 18 and 19 are exothermic, with enthalpy changes of about -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 Ti⁺(CH₃OD)ₙ is the insertion of the Ti⁺ ion into the O-D bond of one of the solvating methanol molecules:

\[ \text{Ti}^+ (\text{CH}_3\text{OD}) \rightarrow [\text{D-Ti}^+-\text{OCH}_3]^+ \rightarrow \text{TiO} + \text{CH}_3\text{D} \quad (20) \]

\[ \rightarrow \text{TiO}^+(\text{OCH}_3) + \text{D} \quad (21) \]

The formation of the TiD⁺ ion via Ti⁺(OCH₃) 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 Ti⁺(OCH₃)ₙ(CH₃OD)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 CH₃OH 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 energies are 93.9 and 92.4 kcal/mol, respectively, which are less than that of the O-H bond. The thermodynamic data show that the C-H bond dissociation energy, however, it is this D elimination reaction that is observed to predominate in the present experiments.

Conclusion

The reactions that proceed within Ti⁺(H₂O)ₙ, Ti⁺(CH₃OCH₃)ₙ, and Ti⁺(CH₃OD)ₙ heterocluster ions were studied using the laser vaporization-molecular beam method. In the reactions of Ti⁺ with water clusters, the formation of TiO⁺ + H₂ is the dominant process. The primary reactions of Ti⁺ ions with CH₃OCH₃ clusters produce a major sequence of cluster ions with the formula Ti⁺(OCH₃)ₙ(CH₃OCH₃)ₙ, which is attributed to the oxidative insertion of Ti⁺ ion into the C-O bond of dimethyl ether followed by CH₃ elimination. Insertions of Ti⁺ ions into the O-D bonds of methanol molecules within the heteroclusters play an important role in producing Ti⁺(OCH₃)ₙ(CH₃OD)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 H₂O or C-O bond of CH₃OCH₃ and CH₃OD, followed by molecular elimination from the [R-Ti⁺-OR] intermediate (R = H or CH₃). 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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