

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

Young-Mi Koo, Hyung-Joon An, Seung-Kyo Yoo,<sup>†</sup> and Kwang-Woo Jung\*

Department of Chemistry and Institute of Basic Science, Wonkwang University, Iksan, Jeonbuk 570-749, Korea

<sup>†</sup>Ace Lab Inc., 104-15 Moonji-dong, Yusung-gu, Daejeon 305-380, Korea

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The intracuster ion-molecule reactions of  $Ti^+(H_2O)_n$ ,  $Ti^+(CH_3OCH_3)_n$ , and  $Ti^+(CH_3OD)_n$  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  $TiO^+(H_2O)_n$  clusters. The mass spectra resulting from the reactions of  $Ti^+$  with  $CH_3OCH_3$  clusters exhibit a major sequence of  $Ti^+(OCH_3)_m(CH_3OCH_3)_n$  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  $Ti^+(OCH_3)_m(CH_3OD)_n$  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.<sup>1-4</sup> 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.<sup>5</sup> 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.<sup>6-9</sup> 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.<sup>10</sup> In studies of the reaction of  $Ti^+$  with water using selected ion drift tube technique<sup>11</sup> and guided ion beam tandem mass spectrometry,<sup>12</sup> 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  $TiO^+$ .<sup>13</sup> 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.<sup>14-17</sup> 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,<sup>18</sup> 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 intracuster 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

\*Corresponding author. E-mail: kwjung@wonkwang.ac.kr

and cluster size also aid the understanding of the influence of solvation on reactions within clusters and the nature of the  $\text{CH}_3$  elimination reactions of the  $\text{Ti}^+$  ion on a molecular level.

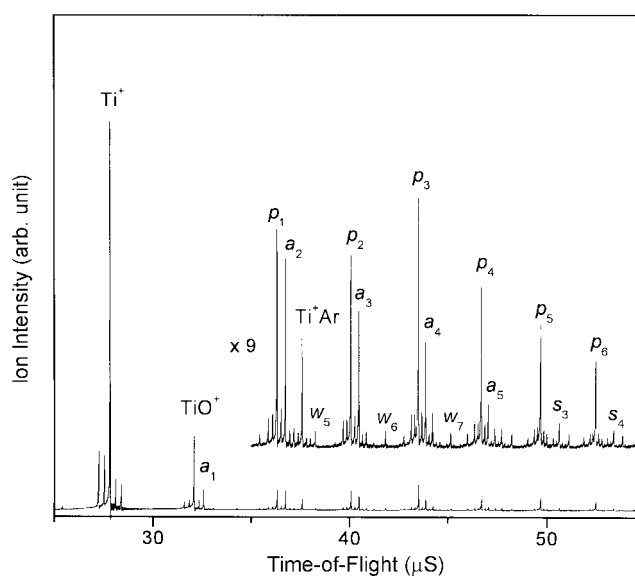
### Experimental Section

A detailed description of the laser vaporization-molecular beam/reflectron time-of-flight mass spectrometer (RTOFMS) has been given previously.<sup>18</sup> 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  $\text{mJ/cm}^2$ . 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  $3 \times 10^{-5}$  and  $5 \times 10^{-7}$  Torr respectively.

Following a delay of typically 50–200  $\mu\text{s}$  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  $\text{H}_2\text{O}$  (99.9%),  $\text{CH}_3\text{OCH}_3$  (>99%), and  $\text{CH}_3\text{OD}$  (>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.

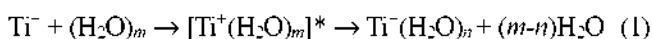
### Results

Figure 1 displays a typical mass spectrum resulting from the reaction of  $\text{Ti}^+$  with  $\text{H}_2\text{O}$  clusters. The spectrum was obtained using a laser pulse energy of 40  $\text{mJ/cm}^2$  and an argon stagnation pressure of 2 atm. We observe pentads of



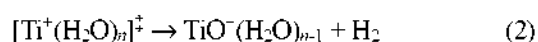
**Figure 1.** Time-of-flight mass spectrum of the cluster ions produced by reactive collisions of laser-ablated  $\text{Ti}^+$  and water clusters seeded in 2 atm Ar. The laser fluence is 40  $\text{mJ/cm}^2$ .  $a_n$ :  $\text{Ti}^+(\text{H}_2\text{O})_n$ ;  $p_n$ :  $\text{TiO}^+(\text{H}_2\text{O})_n$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

peaks corresponding to the natural abundances of the isotopes of titanium ( $^{46}\text{Ti}$ , 8.0%;  $^{47}\text{Ti}$ , 7.3%;  $^{48}\text{Ti}$ , 73.8%;  $^{49}\text{Ti}$ , 5.5%;  $^{50}\text{Ti}$ , 5.4%).<sup>19</sup> 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  $\text{Ti}^+$  and water clusters, possibly followed by evaporation of water molecules:



The evaporation of  $\text{H}_2\text{O}$  results from the excess kinetic energy of the  $\text{Ti}^+$  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.<sup>20,21</sup>

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

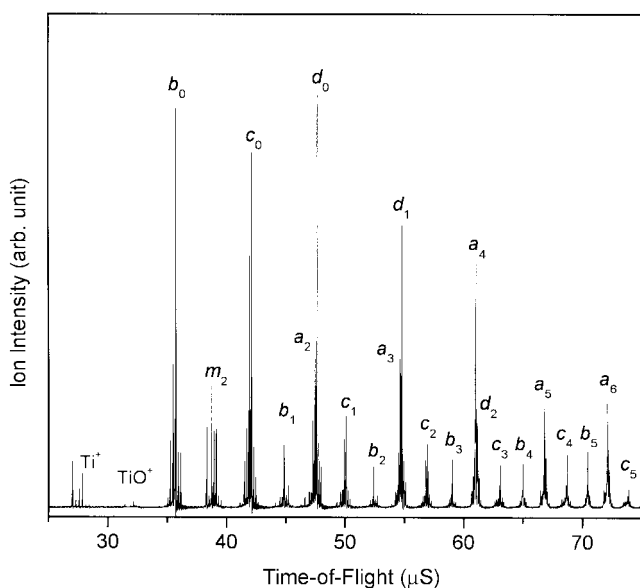


A reaction of this type has been recently observed in a gas phase ion-molecule reaction of  $\text{Ti}^+$  with  $\text{H}_2\text{O}$  at thermal energies.<sup>11</sup> The formation of  $\text{TiO}^+$  is not surprising given the fact that  $\text{Ti}^+$  forms very strong bonds with oxygen atoms.<sup>22</sup> One might speculate that the  $\text{TiO}^+$  ions arise from the Ti target. Prior to the seeding of the  $\text{H}_2\text{O}$  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  $\text{Ti}^-$  and  $\text{Ti}^- \text{Ar}_n$  ( $n = 1-20$ ), with no evidence of other metal oxides or metal clusters, demonstrating that  $\text{TiO}^+$  ions are not produced from the Ti target. In addition, when the water vapor was combined with the Ar carrier gas, a reproducible  $\text{TiO}^+$  ion signal was observed during the repeated laser-vaporization pulses on the Ti target. This provides additional support for the suggestion that  $\text{TiO}^-$  forms through the reaction of  $\text{Ti}^-$  with water clusters.

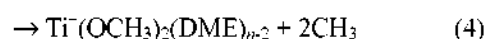
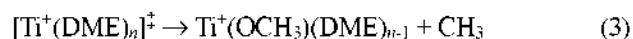
The observation in the mass spectrum of a sequence corresponding to ions of formula  $\text{TiO}_3^-(\text{H}_2\text{O})_n$  (labeled  $s_n$ ) is particularly intriguing. This implies that  $\text{TiO}^+$  ion produced in reaction 2 reacts further in sequential dehydrogenation reactions with  $\text{H}_2\text{O}$  molecules to form  $\text{TiO}_3^+$ . The formation of higher-order oxides through sequential addition of  $\text{O}_2$  to titanium monoxide ion was observed in a recent study of the gas-phase reactions of transition-metal ions with molecular oxygen.<sup>23</sup> The same workers have also shown that  $\text{VO}^+$  sequentially forms  $\text{VO}_3^-$ ,  $\text{VO}_5^+$ , and  $\text{VO}_7^+$  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.<sup>24</sup> We propose that the production of  $\text{TiO}_3^+$  ions is due to the effective insertion capability of  $\text{Ti}^-$  ion into  $\text{H}_2\text{O}$  molecules, as reflected by the large exothermicity of this reaction.

Figure 2 displays a typical TOF mass spectrum of the products of reaction between  $\text{Ti}^-$  and dimethyl ether clusters. The spectrum was obtained using a laser pulse energy of 30 mJ/cm<sup>2</sup> and an argon stagnation pressure of 1.5 atm. Dimethyl ether (DME),  $\text{CH}_3\text{OCH}_3$ , can be looked upon as an  $\text{H}_2\text{O}$  molecule in which the two H atoms are substituted by  $\text{CH}_3$ . The spectrum in the low mass region consists of methoxy-



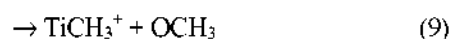
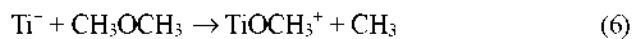
**Figure 2.** Time-of-flight mass spectrum showing the product ions from the reactions of  $\text{Ti}^-$  with dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) clusters.  $a_n$ :  $\text{Ti}^+(\text{DME})_n$ ;  $b_n$ :  $\text{Ti}^+(\text{OCH}_3)(\text{DME})_n$ ;  $c_n$ :  $\text{Ti}^+(\text{OCH}_3)_2(\text{DME})_n$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

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  $\text{OCH}_3$  group is thought to be covalently bonded to the titanium ion. The prevalence of methoxy-rich fragment ions in the mass spectrum indicates that  $\text{CH}_3$  elimination is the preferred decomposition pathway in the reaction of  $\text{Ti}^+$  ion with  $\text{CH}_3\text{OCH}_3$  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,  $\text{Ti}^-$  first inserts into the C-O bond to form  $[\text{CH}_3-\text{Ti}^--\text{OCH}_3]$  after which  $\text{Ti}^-\text{OCH}_3$  is formed *via*  $\text{CH}_3$  elimination. Further reactions of  $\text{Ti}^-\text{OCH}_3$  with solvated  $\text{CH}_3\text{OCH}_3$  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  $\text{CH}_3$  elimination in  $\text{CH}_3\text{OCH}_3$  by the  $\text{Ti}^+$  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.*<sup>25</sup> have reported that  $\text{Fe}^+$  reacts with dimethyl ether to produce  $\text{Fe}(\text{CH}_2\text{O})^-$  and  $\text{CH}_4$  through a mechanism involving metal insertion into the polar C-O bond followed by a  $\beta$ -hydride shift from the alkoxy ligand. Similarly, ion-molecule reactions of  $\text{Ti}^+$  with  $\text{CH}_3\text{OCH}_3$  *via* C-O bond insertion can be represented by the following reactions:



The observation of  $\text{TiOCH}_3^+$ ,  $\text{TiOCH}_2^+$ , and  $\text{TiO}^+$  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  $\text{TiH}^+$  that result from C-H bond insertion are not observed, suggesting that the insertion of  $\text{Ti}^-$  into the C-O bond prevails over insertion into the C-H bond of  $\text{CH}_3\text{OCH}_3$ . The reason for this preference is addressed in detail later in this paper.

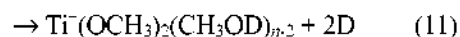
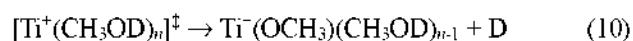
Another interesting feature of the mass spectrum shown in Figure 2 is that the chemical reactivity of the  $\text{Ti}^-$  ion within the heterocluster is greatly influenced by the cluster size. The intensities of the  $\text{Ti}^-(\text{DME})_n$  cluster ions are much lower than those of the  $\text{Ti}^+(\text{OCH}_3)_3(\text{DME})_{n-2}$  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.<sup>26</sup> 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  $\text{Mg}^+$  clusters, the results presented here show that the reactivity of the  $\text{Ti}^+$  ion diminishes with increasing solvation by dimethyl ether molecules. This apparent quenching of  $\text{CH}_3$  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  $\text{CH}_3$  elimination. Because the capability of  $\text{CH}_3$  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  $\text{CH}_3$  radical eliminated from  $\text{CH}_3\text{OCH}_3$  is expected to increase with cluster size.<sup>27</sup> Such an increase in trapping probability would be expected to suppress  $\text{CH}_3$  elimination reactions in sufficiently large clusters.

The substitution of one H atom in  $\text{H}_2\text{O}$  by the more bulky  $\text{CH}_3$  group is expected to alter the reaction pathways because the resulting molecule,  $\text{CH}_3\text{OH}$ , 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  $\text{Ti}^+$  toward the insertion reactions of three different chemical bonds. In addition, isotope substitution experiment using deuterated methanol,  $\text{CH}_3\text{OD}$ , 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  $\text{CH}_3$  group or to sequential eliminations of D from OD groups within the heteroclusters. The mass spectrum obtained from the reactions of  $\text{Ti}^+$  with  $(\text{CH}_3\text{OD})_n$  obtained with a laser pulse energy of  $15 \text{ mJ/cm}^2$  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

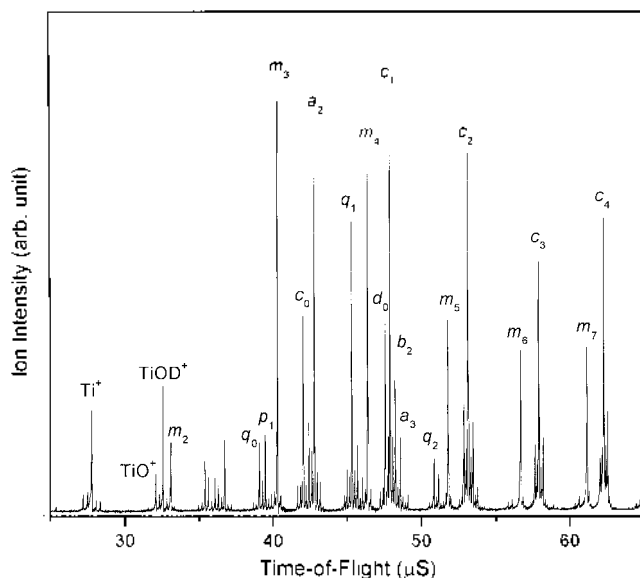
can be attributed to protonated clusters formed by the protonation of the generated parent cluster ions. In the high mass region of the spectrum, the dominant cluster ions consist of a series of heterocluster ions of  $\text{Ti}^+(\text{OCH}_3)_m(\text{CH}_3\text{OD})_{n-m}$  ( $m = 1-3$ ) produced by intracuster 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,<sup>27</sup> who claim that the hydrogen atom elimination channel of  $\text{Mg}^+$  with methanol clusters leads to product ions with apparent stoichiometry  $\text{MgOCH}_3^+(\text{CH}_3\text{OH})_n$ .

Similar to the reactions of  $\text{Ti}^+$  with  $\text{CH}_3\text{OCH}_3$ , these ions can be interpreted as resulting from sequential D elimination reactions:

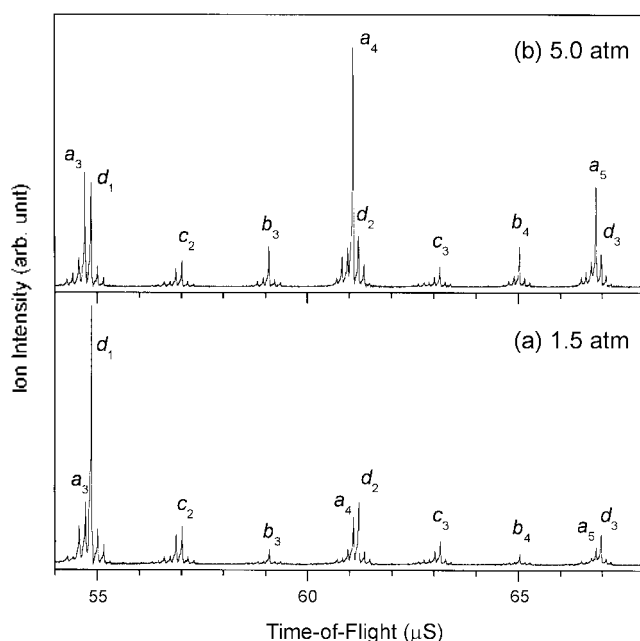


These D elimination reactions occur for up to three methanol molecules, which is similar to the behavior observed for the  $\text{Ti}^+ + \text{CH}_3\text{OCH}_3$  system.  $\text{Ti}^+$  insertion into the C-H, C-O, and O-D bonds of a methanol molecule leads to three intermediates:  $[\text{H-Ti}^+-\text{CH}_2\text{OD}]$ ,  $[\text{DO-Ti}^+-\text{CH}_3]$ , and  $[\text{D-Ti}^+-\text{OCH}_3]$ . Given that  $\text{Ti}^+-\text{OCH}_3$  is the dominant ionic product observed in the present experiments, it is therefore clear that the insertion of  $\text{Ti}^+$  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  $\text{TiO}^+$  and  $\text{TiOD}^+$  ions is primarily attributable to the elimination of  $\text{CH}_3\text{D}$  and  $\text{CH}_3$  from the  $[\text{DO-Ti}^+-\text{CH}_3]$  intermediate formed by  $\text{Ti}^+$  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  $\text{Mg}^+$ ,<sup>28</sup>  $\text{Fe}^+$ ,<sup>29</sup> and  $\text{Sr}^+$ ,<sup>30</sup> and has been found to coincide with the elimination of  $\text{CH}_3$ . Since the  $\text{CH}_3\text{-OH}$  bond energy is  $92.4 \text{ kcal/mol}$ <sup>19</sup> and the binding energy of  $\text{Ti}^+-\text{OH}$  is  $111.1 \text{ kcal/mol}$ ,<sup>31</sup> 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  $18.7 \text{ kcal/mol}$ . 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.<sup>32</sup> 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  $\text{TiO}^+$  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  $\text{Ti}^+$  with  $\text{CH}_3\text{OD}$  seeded in 1 atm Ar. The laser fluence is  $15 \text{ mJ/cm}^2$ .  $a_n$ :  $\text{Ti}^+(\text{CH}_3\text{OD})_n$ ;  $b_n$ :  $\text{Ti}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_n$ ;  $c_n$ :  $\text{Ti}^+(\text{OCH}_3)_2(\text{CH}_3\text{OD})_n$ ;  $d_n$ :  $\text{Ti}^+(\text{OCH}_3)_3(\text{CH}_3\text{OD})_n$ ;  $p_n$ :  $\text{TiO}^+(\text{CH}_3\text{OD})_n$ ;  $q_n$ :  $\text{TiO}^+(\text{OCH}_3)(\text{CH}_3\text{OD})_n$ ;  $m_n$ :  $(\text{CH}_3\text{OD})_n\text{D}^+$ .



**Figure 4.** Time-of-flight mass spectra resulting from the reactions of  $\text{Ti}^-$  with  $\text{CH}_3\text{OCH}_3$  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  $\text{CH}_3\text{OCH}_3$ .

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  $\text{CH}_3\text{OCH}_3$  vapor seeded in 1.5 atm argon is expanded, the  $\text{CH}_3$ ,  $2\text{CH}_3$ , and  $3\text{CH}_3$  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  $3\text{CH}_3$  elimination process dominating. This implies that the intracuster ion-molecule reactions of  $\text{Ti}^+$  with dimethyl ether clusters readily occur in these clusters. As the argon stagnation pressure is increased, however, the solvation of  $\text{Ti}^+$  ions by neutral  $\text{CH}_3\text{OCH}_3$  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  $\text{Ti}^-$  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  $\text{Ti}^-$  with  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OCH}_3$ , and  $\text{CH}_3\text{OH}^a$

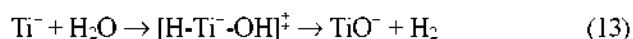
Reactant	Insertion Site	Reaction Products	Enthalpy (kcal/mol)
$\text{H}_2\text{O}$	O-H Bond $\rightarrow$	$\text{TiO}^- + \text{H}_2$	-42.5
		$\text{TiOH}^+ + \text{H}$	8.2
		$\text{TiH}^- + \text{OH}$	65.1
$\text{CH}_3\text{OCH}_3$	C-O Bond $\rightarrow$	$\text{TiO}^- + \text{C}_2\text{H}_6$	-76.4
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

<sup>a</sup>Reaction enthalpies are calculated from the thermochemical data provided in Refs. 19, 33, and 34. <sup>b</sup>The bond energy  $D_0(\text{Ti}^+-\text{OCH}_3)$  is assumed to be equal to  $D_0(\text{Ti}^+-\text{OH})$ . <sup>c</sup>The 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  $\text{CH}_3$  elimination reactions are highly dependent on the argon concentration within the clusters, which is consistent with our previous studies of the reactions of  $\text{Ti}^-$  with  $\text{CH}_3\text{OH}$  clusters.<sup>18</sup>

## Discussion

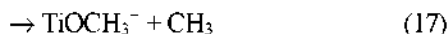
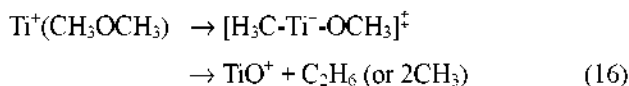
Water molecules contain only one type of O-H chemical bond that might permit the insertion of a  $\text{Ti}^-$  ion. Thus, ion-molecule reactions within  $\text{Ti}^-(\text{H}_2\text{O})_n$  clusters appear to have three possible elimination channels.



The enthalpies of these ion-molecule reactions, estimated from thermochemical data,<sup>19,33,34</sup> 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  $\text{Ti}^-\text{-H}$  or  $\text{Ti}^-\text{-OH}$  bond fission, respectively. The complete absence of  $\text{TiOH}^+$  and  $\text{TiH}^-$  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  $\text{TiO}^-$  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.<sup>12</sup> 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  $\text{H}_2$ .<sup>33</sup> We note that because  $\text{Ti}^-$  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  $\text{Ti}^+$  inserts into the C-H bond to form the intermediate  $[\text{H-Ti}^+-\text{CH}_2\text{OCH}_3]$ , the product ions  $\text{TiH}^+$  or  $\text{Ti}^+-\text{CH}_2\text{OCH}_3$  are expected to form through  $\text{Ti}^+-\text{C}$  or  $\text{Ti}^+-\text{H}$  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  $\text{Ti}^+-\text{H}$  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,<sup>34</sup> which is less than that of the  $\text{H-CH}_2\text{OCH}_3$  bond (ca. 94 kcal/mol). Thus, insertion of  $\text{Ti}^+$  ion into C-O bond seems more energetically favorable than insertion into C-H bond. The C-O insertion reaction of the  $\text{Ti}^+$  ion produces  $\text{TiO}^+$  and  $\text{TiOCH}_3^+$  ions, which are in fact observed in the present experiments. These reactions within the heterocluster ions are summarized as follows.

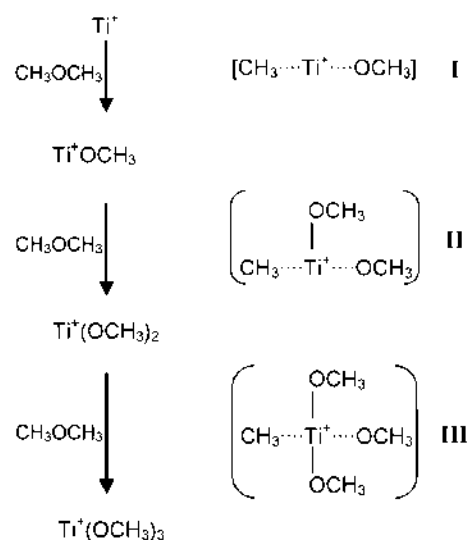


The enthalpy changes of reactions 16 and 17 show exothermicities of  $-76.4$  and  $-28.3$  kcal/mol respectively, suggesting that these reactions will occur as they become energetically feasible.

Similar to the mechanism of the  $\text{Ti}^+ + \text{H}_2\text{O} \rightarrow \text{TiO}^+ + \text{H}_2$  reaction, the  $\text{TiO}^+$  formation channel can proceed from the  $[\text{H}_3\text{C-Ti}^+-\text{OCH}_3]$  intermediate through a four-centered transition state. The  $\text{TiO}^+$  ion can also be produced from the intermediate by  $\beta$ -methyl radical transfer to the metal ion, forming  $\text{C}_2\text{H}_6$ , which is then lost as a neutral product. However, the fact that only minor contributions from  $\text{TiO}^+$  ions are evident in the mass spectra demonstrates that the  $\text{C}_2\text{H}_6$  elimination pathways (either *via* a four-centered transition state or  $\text{CH}_3$  migration) are less efficient routes than the  $\text{CH}_3$  elimination channel (reaction 17) for producing  $\text{Ti}^+(\text{OCH}_3)_n(\text{CH}_3\text{OCH}_3)_n$  ions, even though the former process is more exothermic than the latter. The predominant formation of  $\text{TiOCH}_3^+$  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  $\text{Ti}^+-\text{CH}_3$  (57.5 kcal/mol)<sup>35</sup> is much lower than that of  $\text{Ti}^+-\text{OCH}_3$  (111 kcal/mol) assuming  $D_0^0$  ( $\text{Ti}^+-\text{OCH}_3$ ) is equal to  $D_0^0$  ( $\text{Ti}^+-\text{OH}$ ).<sup>31</sup>

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  $\text{Ti}^+$  with the dimethyl ether moiety.

With the stabilizing environs of a heterocluster, the reaction is initiated by  $\text{Ti}^+$  insertion into a C-O bond of one

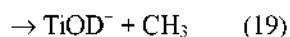


Scheme 1

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*  $\text{CH}_3$  elimination, with the  $\text{OCH}_3$  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,<sup>36-38</sup> 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  $\text{Mg}^+-\text{OCH}_3$  (67.35 kcal/mol)<sup>37</sup> is known to be much stronger than that of  $\text{Mg}^+-\text{CH}_3\text{OCH}_3$  (38.3 kcal/mol).<sup>39</sup> Thus, the bonding in the  $\text{Ti}^+\text{OCH}_3$  ion is likely to resemble covalent rather than electrostatic binding. Similarly, insertion of the  $\text{Ti}^+\text{OCH}_3$  ion into a second dimethyl ether molecule, followed by  $\text{CH}_3$  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  $\text{OCH}_3$  groups around a  $\text{Ti}^+$  ion greatly reduces the ability of  $\text{Ti}^+$  to break the C-O bond of additional dimethyl ether molecules. Because the  $\text{Ti}^+$  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  $\text{TiCl}_4$  and  $\text{Ti}(\text{OR})_4$ , where  $\text{R} = \text{CH}_3$ , isopropyl, and *tert*-butyl.

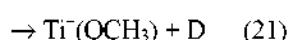
We now consider the reactions of the  $\text{Ti}^+$  ion with methanol clusters. The intracuster reaction of  $\text{Ti}^+(\text{CH}_3\text{OD})_n$  appears to have three elimination channels open, D,  $\text{CH}_3$ , and  $\text{CH}_2\text{D}$  elimination, with D-elimination predominating. There are three types of chemical bonds in a methanol molecule that might permit the insertion of a  $\text{Ti}^+$  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  $\text{Ti}^-$  with dimethyl ether clusters. The C-O insertion reactions of the  $\text{Ti}^+$  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  $\text{TiOD}^+$  and  $\text{TiO}^+$  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  $\text{Ti}^-$  ion into the O-D bond of one of the solvating methanol molecules:



The formation of the  $\text{TiD}^+$  ion *via*  $\text{Ti}^-$ - $\text{OCH}_3$  bond rupture is unfavorable due to the relatively low dissociation energy ( $53.9$  kcal/mol)<sup>40</sup> of the Ti-D bond.  $\text{TiO}^+$  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  $\text{TiO}^+$  to reaction 18 or 20. The lower intensity of the  $\text{TiO}^+$  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  $\text{TiO}^+$  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  $\text{CH}_3\text{OH}$  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).<sup>41</sup> Likewise, C-H and C-O bond dissociation reactions seem more energetically facile than the O-D insertion reaction in the case of  $\text{CH}_3\text{OD}$ . 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  $\text{CH}_3\text{OD}$  is compensated for by the formation of a  $\text{Ti}^-$ - $\text{OCH}_3$  bond. The binding energy of  $\text{Ti}^-$ - $\text{OCH}_3$  is not available. However, considering that  $\text{CH}_3$  is more polarizable than H and that this polarizability would increase the ligand contribution to the bonding,<sup>42</sup> we expect the binding energy of  $\text{Ti}^-$ - $\text{OCH}_3$  to be larger than that of  $\text{Ti}^-$ -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  $\text{Ti}^-$ - $\text{OCH}_3$  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  $\text{Ti}^-$  with water clusters, the formation of  $\text{TiO}^+ + \text{H}_2$  is the

dominant process. The primary reactions of  $\text{Ti}^-$  ions with  $\text{CH}_3\text{OCH}_3$  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  $\text{Ti}^+$  ion into the C-O bond of dimethyl ether followed by  $\text{CH}_3$  elimination. Insertions of  $\text{Ti}^-$  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  $\text{Ti}^-$  ion were found to occur for up to three precursor molecules. The formation of  $\text{TiO}^+$  ion is interpreted as arising from the insertion of  $\text{Ti}^-$  ions into the O-H bond of  $\text{H}_2\text{O}$  or C-O bond of  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{OD}$ , followed by molecular elimination from the  $[\text{R-Ti}^--\text{OR}]$  intermediate ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ). From these observations, we conclude that the chemical reactivity of  $\text{Ti}^+$  ion toward the three different chemical bonds in methanol is in the order  $\text{O-H} > \text{C-O} > \text{C-H}$ . The chemical reactivity of  $\text{Ti}^-$  ions within the heteroclusters decreases with increasing cluster size and increasing argon stagnation pressure.

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