

Chemical Reactivity of Ti⁺ Ion within Ti⁺(CH₂FCH₂OH)_n Clusters

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The ion-molecule reactions that proceed inside Ti⁺(CH₂FCH₂OH)_n heterocluster ions were studied using a laser ablation-molecular beam/reflectron time-of-flight mass spectrometric technique. The mass spectra exhibit a major sequence of cluster ions with the formula Ti⁺(OCH₂CH₂F)_m(CH₂FCH₂OH)_n (*m* = 1, 2), which is attributed to sequential insertions of Ti⁺ into the O-H bond of ethanol molecules within the heteroclusters, followed by H elimination. The TiO⁺ and TiFOH⁺ ions produced from the reactions of Ti⁺ with CH₂FCH₂OH are interpreted as arising from insertion of Ti⁺ into the C-O bond, followed by C₂H₅F and C₂H₄ elimination, respectively. The observation of Ti⁺(H₂O)(CH₂FCH₂OH)_n ions is attributed to the insertion of Ti⁺ ions into the C-O bond in the ethanol molecules, leading to a β-H atom transfer and CH₂CHF elimination. This reaction pathway presumably plays an important role as the cluster size increases. *Ab initio* calculations on the complexes of Ti⁺ with CH₂FCH₂OH molecules show that the minimum energy structure is that in which Ti⁺ is attached to the O and F atoms of fluorinated ethanol, forming a five-membered ring. The formation mechanisms and reaction energetics of the observed heterocluster ions are discussed.

Key Words : Ion-molecule reaction, Titanium, 2-Fluoroethanol, Heterocluster

Introduction

Recent investigations on ion-molecule reactions of metal ions in the gas phase have yielded useful information not only on the structures of the complexes but also on the energetics and dynamics of the reactions between metal ions and molecules.¹⁻⁶ However, studies of metal ion-ligand interactions, which are important in a wide range of biological, chemical, and physical processes, are often complicated by the heterogeneity of the system. Mass spectrometric studies of gas-phase ion-molecule reactions can provide quantitative information regarding the intrinsic chemical and physical properties of transition metal ions while avoiding complicated solvent phenomena.⁷⁻⁹ Such gas-phase studies have enhanced our understanding of the behavior of transition metal ions in the condensed phase.

During the past few years, we have reported our findings on the intracuster ion-molecule reactions of Ti⁺ with various organic molecules.¹⁰⁻¹³ This has enabled us to elucidate the reactivity of the Ti⁺ ion and dissociation pathway dynamics of the heterocluster complexes. For example, the Ti⁺ ion tends to activate the C-O bond of an ROH molecule (R = methyl, ethyl, *t*-butyl) to form an HO-Ti⁺-R intermediate, which then loses RH and R to produce TiO⁺ and TiOH⁺, respectively.¹² Sequential insertions of Ti⁺ into the O-H bond of ROH molecules within the heteroclusters were found to play a predominant role in producing Ti⁺(OR)_m(ROH)_n ions (*m* = 1-3). The intracuster ion-molecule reactions of Ti⁺ with ether clusters, (CH₃OR)_n (R = CH₃, *n*-C₃H₇, *n*-C₄H₉, *t*-C₄H₉), indicate the formation of major sequences of heterocluster ions with the formula Ti⁺(OCH₃)_x(OR)_y(CH₃OR)_n, where *x* = 1-3 and *y* = 0-2.¹³ These sequences are attributed

to the insertion of Ti⁺ ions into the C-O bonds of the ether molecules within the heteroclusters, followed by alkyl radical elimination, although the C-H and C-C bond interactions become more favorable as the size of the alkyl group in the ether molecule increases.

Despite the many studies on the reactions of Ti⁺ with small molecules, few studies have examined the mechanism and energetics of the reactions of Ti⁺ with molecules possessing more than one functional group. In this respect, a more quantitative investigation of these reaction products is important to understand the reaction mechanism. A study of the specific chemical dynamics of reactions within cluster ions also provides valuable information on the changes in the reaction pathways with increasing cluster size, which reflect the transition from gas-phase to solution-phase reactions.¹⁴⁻¹⁷

In the work reported here, we extended our recent study on the reactivity of Ti⁺ ions with respect to the breaking of the various chemical bonds of 2-fluoroethanol.¹⁸ Because this compound possesses highly electronegative F atoms and -OH, they provide good models for unraveling the influence of fluorine substituents on the chemical reactivity of Ti⁺. A good approach to studying the influence of the fluorine substituents is to examine the effect of selectively activating the different bonds in the molecule. To probe the cluster reactivity, we examined the reactions using a combination of laser ablation and supersonic gas expansion. Studies of the reactivity of titanium heteroclusters as a function of cluster size were also performed to help elucidate the influence of solvation on reactions within clusters and the nature of the H-elimination reactions of the Ti⁺ ion at the molecular level. In addition, *ab initio* and density functional calculations

were carried out to determine the structures and binding energies of the relevant Ti^+ - $\text{CH}_2\text{FCH}_2\text{OH}$ reaction products.

Experimental Section

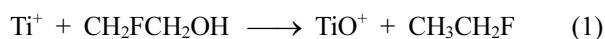
Experiments. Details of the apparatus used for the present experiments have been given previously;¹⁰ therefore, only a brief introduction is presented here. A rotating titanium disk was mounted 2 cm downstream from the exit of a pulsed valve. The sample disk was rotated and translated simultaneously by a step motor on each laser pulse to expose fresh surfaces during the laser-ablation experiments. The pulsed valve was employed to generate beams of alcohol clusters by supersonic expansion of the vapor seeded in argon with a backing pressure of 1–2 atm through a 0.5 mm diameter orifice. After opening the solenoid valve, the third harmonic (355 nm) of an Nd:YAG laser ($\sim 50 \text{ mJ/cm}^2$) was partially focused on the Ti disk with a spot size of $\leq 1 \text{ mm}^2$ for the generation of metal cations. The laser-ablated species containing metal ions and atoms traversed perpendicularly to the supersonic jet stream 1 cm from the ablation sample target, where they reacted with the reactant clusters. The resulting ion complexes were then skimmed by a skimmer of diameter 1 mm and cooled collisionally as they traveled 10 cm downstream to the extraction region of the reflectron time-of-flight mass spectrometer (RTOFMS). The distance between the nozzle and skimmer was 4 cm.

The positive ions were extracted by applying a high-voltage pulse in a single-stage extractor, and they then traveled along a field-free region of length 1 m. They were then reflected using a double-stage reflectron 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 mass spectrum was recorded using a 500 MHz digital oscilloscope coupled to a personal computer. Spectrophotometric grade $\text{CH}_2\text{FCH}_2\text{OH}$ (95%) and $\text{C}_2\text{H}_5\text{OH}$ (> 99.5%) (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.

Computations. The ground-state geometry of the $\text{Ti}^+ \cdots \text{CH}_2\text{FCH}_2\text{OH}$ complexes and related reaction products were fully optimized at the B3LYP/6-311++G(d,p) level using the Gaussian 03W program,¹⁹ which includes Becke's three-parameter nonlocal hybrid exchange functional and the non-local correlation functional of Lee, Yang, and Parr.²⁰ Two starting structures of the $\text{Ti}^+ \cdots \text{CH}_2\text{FCH}_2\text{OH}$ complex were used in our calculations: one with the Ti^+ attached to the F atom, and the other with the Ti^+ attached between the O and F atoms. The binding energy of the complex was calculated from the difference between the total energy of the complex in its optimized ground-state geometry, $E(\text{Ti}^+ \cdots \text{CF}_2\text{FCH}_2\text{OH})$, and the total energies of Ti^+ and $\text{CH}_2\text{FCH}_2\text{OH}$ as separate entities, $E(\text{Ti}^+) + E(\text{CH}_2\text{FCH}_2\text{OH})$. To obtain the reaction energies for the $\text{Ti}^+ + \text{CH}_2\text{FCH}_2\text{OH}$ system, the reaction products were also fully optimized at the same level. Zero-point-energy corrections were included when calculating the reaction energies.

Results and Discussion

2-Fluoroethanol (FE) is an interesting molecule because it possesses two functional groups, namely, an F atom and an OH group. Substitution on the methyl group in ethanol with a highly electronegative F atom is expected to alter the reaction pathways, offering an opportunity to investigate the chemical reactivity of Ti^+ in the insertion reactions observed for ethanol. A typical mass spectrum of the products of the reaction between Ti^+ and FE clusters is displayed in Figure 1. We observed pentads of peaks corresponding to the natural abundances of the Ti isotopes (^{46}Ti , 8.0%; ^{47}Ti , 7.3%; ^{48}Ti , 73.8%; ^{49}Ti , 5.5%; ^{50}Ti , 5.4%). Unless otherwise noted, the results presented below refer to complexes involving the most abundant isotope. In the low-mass region (Figure 1a), the reaction products consist of TiO^+ ($m/z = 64$) and TiFOH^+ ($m/z = 84$) produced by ion–molecule reactions of Ti^+ and FE. These fragment ions are attributed to the following reactions.



Titanium has a lower ionization energy (IE) than FE (IE = 6.82 eV for Ti and 10.66 eV for $\text{CH}_2\text{FCH}_2\text{OH}$);²¹ hence, once the complex is formed, the positive charge in the heterocluster is expected to reside on the Ti. The formation of TiO^+ via reaction 1 is not surprising in the sense that Ti^+ bonds very strongly to oxygen atoms.²² $\text{TiO}^+ + \text{CH}_3\text{CH}_2\text{F}$ products arise from the $[\text{HO-Ti}^+-\text{CH}_2\text{CH}_2\text{F}]$ intermediate by hydrogen migration to form an $\text{OTi}^+(\text{H})(\text{CH}_2\text{CH}_2\text{F})$ transition state, followed by elimination of $\text{CH}_3\text{CH}_2\text{F}$.

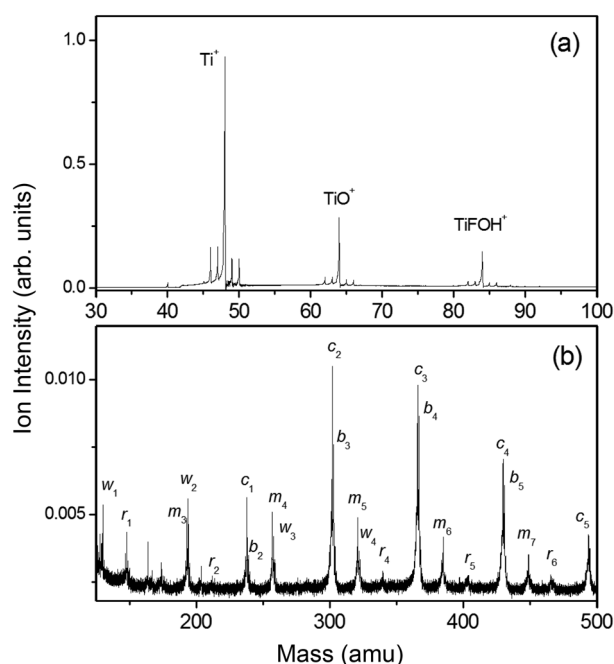
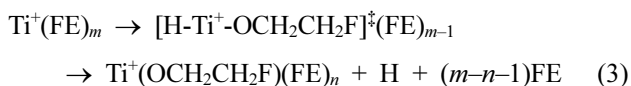


Figure 1. Mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti^+ and 2-fluoroethanol (FE) clusters seeded in 1.7 atm Ar. b_n : $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})(\text{FE})_n$; c_n : $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$; m_n : $(\text{FE})_n\text{H}^+$; r_n : $\text{TiFOH}^+(\text{FE})_n$; w_n : $\text{Ti}^+(\text{H}_2\text{O})(\text{FE})_n$.

Unlike the Ti⁺ + C₂H₅OH system studied previously by our group,¹² in which TiOH⁺ ions were generated by insertion of Ti⁺ ions into the C-O bonds of C₂H₅OH molecules, the TiOH⁺ ion is not observed among the products of the reaction of Ti⁺ and FE. This implies that rupturing the Ti⁺-C bond of the [HO-Ti⁺-CH₂CH₂F] intermediate in the reaction of Ti⁺ + FE is less efficient than other product channels, presumably due to the different geometry of the Ti⁺⋯FE complex compared with that of the Ti⁺⋯C₂H₅OH complex. Recently, Yang *et al.* reported that the Mg⁺⋯CF₃CH₂OH complex has a five-membered ring structure, in which Mg⁺ attaches to both the O and one of the three F atoms of CF₃CH₂OH.²³ Thus, the current observation that TiFOH⁺ ions are formed in substantial quantities in the reaction of Ti⁺ with FE strongly suggests that the reaction proceeds *via* a five-membered Ti⁺⋯FE complex. Similar examples are the reactions of Fe⁺ + ClCH₂CH₂Br and Co⁺ + ClCH₂CH₂OH, in which the metal ion interacts with both functional groups in a five-membered ring configuration, leading to the formation of FeClBr⁺ and CoClOH⁺ by elimination of ethylene.²⁴ The observation in the mass spectrum of minor signals corresponding to TiFOH⁺(FE)_n (*r*_n series in Figure 1b) cluster ions, however, demonstrates that reaction 2 is less favorable within the large heteroclusters.

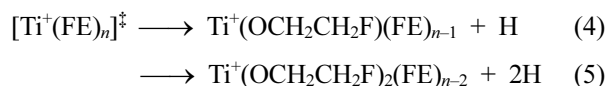
The prominent peaks in the high-mass region of the spectrum consist of cluster ions with formulas Ti⁺(OCH₂CH₂F)(FE)_n (denoted *b*_n), Ti⁺(OCH₂CH₂F)₂(FE)_n (denoted *c*_n), (FE)_nH⁺ (denoted *m*_n), and Ti⁺(H₂O)(FE)_n (denoted *w*_n). (FE)_nH⁺ cluster ions can be attributed to the intracuster protonation of the parent (FE)_n⁺ ions formed in the region where the laser-ablated plume and supersonic FE cluster beam intersect. The Ti⁺(OCH₂CH₂F)(FE)_n and Ti⁺(OCH₂CH₂F)₂(FE)_n product ions, formed from the H-elimination reactions of the intact Ti⁺(FE)_n cluster ions, are observed with up to 10 ethanol units in the present experiments. The observation of ethoxy-rich fragment ions implies that the Ti⁺ ion readily reacts with FE molecules solvated within heteroclusters. Similar to the reactions between Ti⁺ and C₂H₅OH clusters, the predominant reaction pathway is characterized by insertions of a Ti⁺ ion into the O-H bond of FE molecules within the parent Ti⁺(FE)_m clusters, followed by H elimination.



The [H-Ti⁺-OCH₂CH₂F][‡] intermediate formed by Ti⁺ insertion can dissociate internally, with the Ti⁺(OCH₂CH₂F) ion being produced *via* H elimination. In this reaction, the OCH₂CH₂F behaves more like a tightly bound group than a solvating ligand species. It has been found that the binding energies of Mg⁺-OCH₃ (67.35 kcal/mol) and Co⁺-OCH₃ (> 69 kcal/mol) are much higher than those of Mg⁺-CH₃OH (37.7 kcal/mol) and Co⁺-CH₃OH (35.28 kcal/mol).^{25,26} Bonding in the Ti⁺-OCH₂CH₂F ion is thus likely to resemble covalent bonding rather than an electrostatic interaction. Formation of the TiH⁺ ion *via* Ti⁺-O bond rupture from the

[H-Ti⁺-OCH₂CH₂F] intermediate is unfavorable because of the relatively low dissociation energy (54.2 kcal/mol) of the Ti-H bond.²⁶

A surprising finding for Ti⁺(OCH₂CH₂F)_m(FE)_n (*m* = 1, 2) cluster ions is that H elimination in FE by the Ti⁺ ion is possible for up to two FE molecules. This process proceeds *via* sequential H-elimination reactions:



Our recent study of the reactions of Ti⁺ with C₂H₅OD clusters, we found that the dominant species are Ti⁺(OC₂H₅)(C₂H₅OD)_n and Ti⁺(OC₂H₅)₂(C₂H₅OD)_n series ions, which can only arise from cleavage of O-D bonds in the association complex Ti⁺(C₂H₅OD)_n.¹² These results support our current conclusion that H elimination due to the Ti⁺ ion (reactions 4 and 5) occurs from separate FE molecules. Within the stabilizing environs of a heterocluster, insertion of a Ti⁺(OCH₂CH₂F) ion into a second FE molecule produces the (CH₂FCH₂O)Ti⁺(H)(OCH₂CH₂F) intermediate. This intermediate then dissociates internally and a Ti⁺(OCH₂CH₂F)₂ ion is produced *via* H elimination.

We calculated the ground-state structures and absolute energies of the Ti⁺⋯FE complexes to interpret the reaction mechanism. To the best of our knowledge, the binding energy of alcohol molecules to Ti⁺ has not been measured or calculated. This is primarily due to the high reactivity of Ti⁺ toward the OH group, which prevents the formation of a complex in which they are directly linked. At long range, the interaction between Ti⁺ and FE species can be considered an ion-dipole attraction. Thus, the Ti⁺⋯FE complex is presumed to correspond to a minimum in the potential energy surface. The optimized structures of an FE molecule and two isomers of the Ti⁺⋯FE complex (referred to as I and II) are depicted in Figure 2, and their values for various parameters, including the total energy, bond lengths, bond angles, and atomic charge of Ti⁺, are listed in Table 1. Complex I represents the case in which the Ti⁺ ion attaches to the F atom of the alkyl group, leading to activation of the C-F bond. When the Ti⁺ ion approaches the F atom of the FE molecule, the molecule undergoes a significant structural change. For example, the C-F bond length is 1.402 Å in a free molecule, whereas in complex I, the C-F bond is stretched to 1.507 Å and the C-H

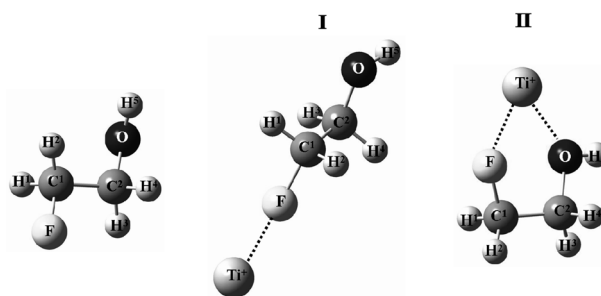


Figure 2. The optimized ground-state structures for a CH₂FCH₂OH molecule and two possible Ti⁺-2-fluoroethanol complexes calculated at the B3LYP/6-311++G(d,p) level.

Table 1. Summary of the B3LYP/6-311++G(d,p) calculations for a CH₂FCH₂OH molecule and the two possible Ti⁺-2-fluoroethanol complexes

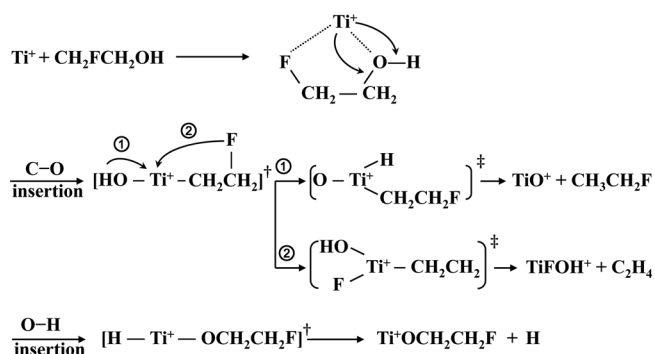
		Bond lengths (Å)		Bond angles (degree)		Atomic charges (Bond strength ^b)		Zero-point vibrational energy ^a
Ti ⁺ (-849.1096913 ^a)		-		-		-		0
CH ₂ FCH ₂ OH (-254.35794365 ^a)		C ¹ -F: 1.402 C ¹ -H ¹ : 1.092 C ¹ -H ² : 1.095 C ¹ -C ² : 1.523	C ² -H ³ : 1.091 C ² -H ⁴ : 1.096 C ² -O: 1.425 O-H ⁵ : 0.962	F-C ¹ -H ¹ : 108.1 H ¹ -C ¹ -H ² : 109.4 C ¹ -C ² -O: 110.8	H ³ -C ² -H ⁴ : 108.1 O-C ² -H ⁴ : 111.9 C ² -O-H ⁵ : 109.2	(C ¹ -F: 109.5) (C ² -O: 91.9) (O-H ⁵ : 106.9) (C ¹ -H: 105.1)	(C ¹ -C ² : 91.4)	0.072841
Complex I (-1103.50928956 ^a)		C ¹ -F: 1.507 C ¹ -H ¹ : 1.087 C ¹ -H ² : 1.086 C ¹ -C ² : 1.514 C ² -H ³ : 1.097	C ² -H ⁴ : 1.096 C ² -O: 1.451 O-H ⁵ : 0.963 F-Ti: 2.042	H ¹ -C ¹ -H ² : 112.7 F-C ¹ -C ² : 107.6 H ³ -C ² -H ⁴ : 109.2	C ¹ -C ² -O: 102.2 C ² -O-H ⁵ : 110.37 C ¹ -F-Ti: 167.64	C ¹ : -0.116 C ² : -0.248 F: -0.175 Ti: 0.716 O: -0.286	H ¹ : 0.237 H ² : 0.222 H ³ : 0.182 H ⁴ : 0.182 H ⁵ : 0.286	0.072783
Complex II (-1103.55485876 ^a)		C ¹ -F: 1.450 C ¹ -H ¹ : 1.089 C ¹ -H ² : 1.088 C ¹ -C ² : 1.507 C ² -H ³ : 1.092	C ² -H ⁴ : 1.091 C ² -O: 1.464 O-H ⁵ : 0.965 F-Ti: 2.240 O-Ti: 2.153	H ¹ -C ¹ -H ² : 110.5 F-C ¹ -C ² : 106.2 H ³ -C ² -H ⁴ : 110.1 C ¹ -C ² -O: 106.1	C ² -O-H ⁵ : 111.3 C ² -O-Ti: 119.8 C ¹ -F-Ti: 115.9 F-Ti-O: 71.73	C ¹ : -0.184 C ² : -0.303 F: -0.130 Ti: 0.718 O: -0.360	H ¹ : 0.245 H ² : 0.215 H ³ : 0.249 H ⁴ : 0.198 H ⁵ : 0.352	0.074666

^aAbsolute energies in Hartrees. ^bUnits are kcal/mol

bonds shrink to 1.086-1.087 Å. The other geometry parameters of the FE unit in this complex resemble those of the free FE molecule. The Ti-F bond length in complex I is calculated to be 2.042 Å, which corresponds to a purely electrostatic bonding.²⁷

Complex II corresponds to the case in which Ti⁺ interacts with both the O and F atoms of the FE molecule, forming a complex containing a five-membered ring. This structure is similar to the intermediates of the Mg⁺ + *o*-C₆H₄F₂, Mg⁺ + CF₃CH₂OH, Fe⁺ + BrCH₂CH₂Cl, and Co⁺ + ClCH₂CH₂OH reactions.^{23,24,28} On going from free FE to complex II, the C-O and C-F bonds are lengthened by 0.039 Å and 0.048 Å, respectively; thus it is likely that this bond weakening caused by Ti⁺ association to form the complex ultimately leads to the rupture of these bonds. As such, the ground-state structure of FE is changed only slightly when both the O and F atoms are coordinated to Ti⁺ to form a five-membered ring complex. Note that structure II is more stable than structure I by 28.6 kcal/mol, suggesting that complex II is the more favorable of the two structures in the experiments carried out in the present work. Moreover, because the Ti⁺ ion in the complex is closer to the O atom (2.15 Å) than to the F atom (2.24 Å), the C-O and O-H bonds appear to be easier to rupture than the C-F bond. The linkage of Ti⁺ to O and F in complex II is consistent with our observation that the insertion reactions of the Ti⁺ ion into the C-O and O-H bonds lead to the facile production of TiO⁺, TiFOH⁺, and Ti⁺(OCH₂-CH₂F)_{*m*}(FE)_{*n*} (*m* = 1, 2) ions.

The observed reaction pathways of Ti⁺ + FE are summarized in Scheme 1 along with the calculated reaction energies. As can be seen from Scheme 1, the ion-molecule reactions of Ti⁺ with FE can be divided into two categories: (i) C-O bond activation (reactions 1 and 2) and (ii) O-H bond activation (reaction 3). Ti⁺ insertion into the C-O bond of an

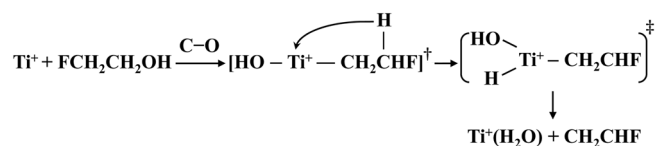
**Scheme 1.** Summary of the observed reaction pathways of Ti⁺ + CH₂FCH₂OH.

FE molecule can lead to a [HO-Ti⁺-CH₂CH₂F] intermediate. This intermediate could undergo α-H atom transfer from the OH group to the Ti⁺ ion, followed by CH₃CH₂F elimination, to produce TiO⁺. This mechanism is analogous to the Ti⁺ + H₂O → TiO⁺ + H₂ reaction, in which the dehydrogenation channel proceeds from a [H-Ti⁺-OH] intermediate by H migration from O to form [H₂-Ti⁺-O] because Ti⁺ has three valence electrons.²⁹ Alternatively, the [HO-Ti⁺-CH₂CH₂F] intermediate could produce TiFOH⁺ followed by transfer of an F atom attached to the β-carbon and elimination of C₂H₄. The present mass spectrometry results, in which TiO⁺ and TiFOH were observed as significant products, are consistent with the calculation results indicating that both the TiO⁺ and TiFOH⁺ product channels are thermodynamically favorable because of their high exothermicity (-107.8 and -148.5 kcal/mol, respectively).

As a major intracluster ion-molecule reaction channel of Ti⁺(FE)_{*n*} heterocluster ions, the Ti⁺ ion can insert into the O-H bond of an FE molecule. It is noteworthy that the

Ti⁺OCH₂CH₂F + H formation channel is clearly observed within the heteroclusters in spite of its small endothermicity (+7.4 kcal/mol). Because Ti⁺(OCH₂CH₂F)(FE)_n and Ti⁺(OCH₂CH₂F)₂(FE)_n ions are the predominant products observed in the present experiments, it is likely that, within the heterocluster ions, insertion of Ti⁺ into the O-H bond to form the [H-Ti⁺-OCH₂CH₂F] intermediate is the most favored reaction channel among the possible insertion routes (*i.e.*, C-O, C-F, and O-H bonds). The dominance of the Ti⁺-OCH₂CH₂F + H product channel over the Ti⁺-H + OCH₂CH₂F channel can be rationalized on the basis that the Ti⁺-OCH₂CH₂F bond is stronger than the Ti⁺-H bond. Qualitatively, the exit channel of Ti⁺OCH₂CH₂F + H formation has the highest energy among the reaction products. By considering the strengths of the bonds in FE (listed in Table 1), the calculated C-O bond activation (91.9 kcal/mol) is energetically favored over activations of the O-H (106.9 kcal/mol) and C-F (109.5 kcal/mol) bonds. However, despite the large O-H bond dissociation energy, this H elimination is observed to predominate in the heterocluster reactions. One possible rationale for this result is that breakage of the O-H bond in FE is compensated by the formation of a strong Ti⁺-OCH₂CH₂F bond and is further stabilized by the solvating molecules.

It is quite surprising that the reaction of Ti⁺ with FE clusters gives rise to Ti⁺(H₂O)(FE)_n ions (*w_n* series) as shown in Figure 1. The [HO-Ti⁺-CH₂CH₂F] intermediate formed from the Ti⁺ insertion into the C-O bond of an FE molecule could decompose to Ti⁺(H₂O) + CH₂CHF by H-atom transfer from the β-carbon (Scheme 2). The enthalpy change shows an exothermic reaction (-30.2 kcal/mol).



Scheme 2. Reaction pathway for the formation of Ti⁺(H₂O) ion along with the calculated reaction energies (kcal/mol).

The H₂O formation pathway is also found in the reactions of Ti⁺ with C₂H₅OH (EtOH) clusters. Figure 3 shows a typical mass spectrum resulting from reaction of the Ti⁺ ion with EtOH clusters. The prominent peaks correspond to the heterocluster ions of Ti⁺(OEt)(EtOH)_n (denoted *b_n*) and Ti⁺(OEt)₂(EtOH)_n (denoted *c_n*), formed from the H-elimination reactions of the Ti⁺(EtOH)_n ions (denoted *a_n*). Unlike the Ti⁺ + CH₂FCH₂OH system, the Ti⁺(EtOH)_n ions are clearly observed among the products of the reaction of Ti⁺ with EtOH clusters. This finding thus indicates that, as far as the intracuster reaction of Ti⁺ with ethanol clusters is concerned, the dominant H-elimination pathway is greatly suppressed by replacing the F atom on ethyl group of ethanol with H atom.

Although of much lower intensity, the fragment ions *w_n* corresponding to Ti⁺(H₂O)(EtOH)_n can be clearly recogni-

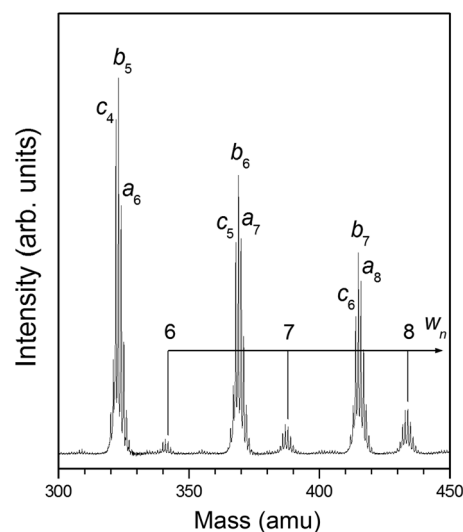


Figure 3. Mass spectrum of the cluster ions produced by the reactions of Ti⁺ with C₂H₅OH (EtOH) clusters. *a_n*: Ti⁺(EtOH)_n; *b_n*: Ti⁺(OEt)(EtOH)_n; *c_n*: Ti⁺(OEt)₂(EtOH)_n; *w_n*: Ti⁺(H₂O)(EtOH)_n.

zed in the mass spectrum. The increasing tendency of the Ti⁺(H₂O)(EtOH)_n ions with cluster size is suggestive of the effective energy dissipation by solvent molecules after the Ti⁺(H₂O)(EtOH)_n ions have formed. Therefore, the result demonstrates that the H₂O formation channel is accompanied by the β-H atom transfer in the reaction of Ti⁺ with an ethanol molecule. This is consistent with the view that the reaction of Ti⁺ with CF₃CH₂OH does not produce Ti⁺(H₂O)-(TFE)_n ions because the CF₃CH₂OH molecule does not possess a β-hydrogen atom, as depicted in Scheme 2.³⁰

Conclusions

In the present study we investigated ion-molecule reactions inside mixed Ti⁺(CH₂FCH₂OH)_n heterocluster ions using a combination of laser ablation and supersonic beam expansion. The observation of TiO⁺ and TiFOH⁺ ions among the reaction products of the reactions of Ti⁺ with CH₂FCH₂OH is explained on the basis of a C-O insertion reaction followed by C₂H₅F and C₂H₄ fragmentations, respectively. The intracuster ion-molecule reactions produce a major sequence of Ti⁺(OCH₂CH₂F)_m(CH₂FCH₂OH)_n ions (*m* = 1, 2), which is attributed to sequential insertions of Ti⁺ into the O-H bond of CH₂FCH₂OH followed by H eliminations. In addition, observation of the Ti⁺(H₂O)(CH₂FCH₂OH)_n ion is interpreted as indicating the occurrence of a C-O bond insertion reaction to form Ti⁺(H₂O) + CH₂CHF by β-H atom transfer, which plays an important role at large cluster sizes. *Ab initio* calculations were carried out to study the structures and binding energies of the association complexes and the relevant reaction products. The reaction pathways and energetics of the proposed mechanisms were presented.

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