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Intracluster Ion−Molecule Reactions of Ti^+ with C_2H_5OH and CF_3CH_2OH Clusters: Influence of Fluorine Substituents on Chemical Reactivity

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A laser ablation−molecular beam/reflectron time-of-flight mass spectrometric technique was used to investigate the ion−molecule reactions that proceed within $Ti^+(ROH)_n$ ($R = C_2H_5$, CF_3CH_2) heterocluster ions. The mass spectra exhibit a major sequence of cluster ions with the formula $Ti^+(OR)_m(ROH)_n$ ($m = 1, 2$), which is attributed to sequential insertions of Ti^+ into the O−H bond of C_2H_5OH or CF_3CH_2OH molecules within the heteroclusters, followed by H eliminations. The TiO^+ and $TiOH^+$ ions produced from the reactions of Ti^+ with C_2H_5OH are interpreted as arising from insertion of Ti^+ into the C−O bond, followed by C_2H_5 and C_2H_6 eliminations, respectively. When Ti^+ reacted with CF_3CH_2OH, by contrast, considerable contributions from $TiFOH^+$, $TiF_2{}^+$, and TiF_2OH^+ ions were observed in the mass spectrum of the reaction products, indicating that F and OH abstractions are the dominant product channels. Ab initio calculations of the complex of Ti^+ with 2,2,2-trifluoroethanol show that the minimum energy structure is that in which Ti^+ is attached to the O atom and one of the three F atoms of 2,2,2-trifluoroethanol, forming a five-membered ring. Isotope-labeling experiments additionally show that the chemical reactivity of heterocluster ions is greatly influenced by the presence of fluorine substituents and cluster size. The reaction energetics and formation mechanisms of the observed heterocluster ions are discussed.

1. Introduction

The importance of chemical reactions induced by the interaction of transition metal ions with hydrocarbon molecules has prompted extensive studies aimed at elucidating the catalytic activity of metal ions, which is important in a wide range of biological, chemical, and physical processes.[1−6] Mass spectrometric studies of gas-phase ion−molecule reactions have yielded quantitative information regarding the intrinsic chemical and physical properties of transition metal ions while avoiding complicated solvent phenomena.[7] Such gas-phase studies have enhanced our understanding of the behavior of transition metal ions in the condensed phase.

The Ti^+ ion is known to activate the C−C, C−H, and O−O bonds in specific gas-phase reactions.[8−12] Castleman et al. reported that insertion reactions of Ti^+ ions with methanol produce TiO^+, $TiOH^+$, $Ti(CH_2O)^+$, and $Ti(CH_3O)^+$ as the primary reaction products.[13] On the basis of results obtained using a laser ablation−molecular beam method, Sato et al.[14] suggested that the elimination of a hydrogen molecule (reaction 1) from the ion−molecule reactions of Ti^+ with methanol clusters is the dominant process producing the fragment ions of formula $Ti^+(CH_3OH)_{n-1}CH_2O$.

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

El-Shall et al. have also reported that the primary product ions $TiO^+(CH_3OCH_3)(CH_3OH)_n$, produced from the reactions of Ti^+ with methanol clusters, can be attributed to the catalytic conversion of methanol dimer into dimethyl ether by TiO^+ (reaction 2).[15]

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

The above results raise the question of whether the Ti^+ ion is first inserted into the methanol molecule and then H_2 elimination occurs (reaction 1), or whether the Ti^+ ion is oxidized to form TiO^+ (reaction 2) within the heteroclusters. We recently reported our findings on the intracluster ion−molecule reactions of the $Ti^+(ROH)_n$ (R = methyl, ethyl, *tert*-butyl) heterocluster ions.[16,17] Consecutive insertions of Ti^+ into the O−H bond of methanol molecules within the heteroclusters were found to play an important role in producing $Ti^+(OR)_m(ROH)_n$ ions ($m = 1−3$). This reaction pathway stands in striking contrast to those proposed previously (reactions 1 and 2). In this respect, more quantitative investigation of these reaction products is important for understanding the reaction mechanism. The 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 reflects the transition from gas-phase to solution-phase reactions.[18−22] Apart from the numerous studies of 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 the present study, we investigated the reactivity of Ti^+ ions with respect to the breaking of the various chemical bonds of ethanol and 2,2,2-trifluoroethanol (TFE). Since TFE possesses

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highly electronegative F atoms and −OH, it provides a good model system 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. In order to probe the cluster reactivity, we examined the reactions using a combination of laser ablation and supersonic gas expansion. Isotope substitution experiments using deuterated TFE were performed to elucidate the reaction mechanisms for precursor activation by Ti^+. In addition, ab initio and density functional theory calculations were carried out to determine the structures and binding energies of the relevant $Ti^+-CF_3CH_2OH$ reaction products. Studies of the reactivity of titanium−alcohol heteroclusters as a function of cluster size were also performed to aid in the understanding of the influence of solvation on reactions within clusters and the nature of the H-elimination reactions of the Ti^+ ion at the molecular level.

2. Methods

2.1. Experiments. The apparatus used for the present experiments was the same as that described previously.[16,17] Briefly, a laser ablation technique combined with a supersonic molecular beam was employed to induce metal ion−molecule reactions. A rotating titanium disk was mounted 2 cm downstream from the exit of a pulsed valve (General Valve, Series 9). Alcohol clusters were formed via the adiabatic expansion of a gas mixture of reactant molecules seeded in argon with a backing pressure of 1−2 atm through a pulsed nozzle. After the solenoid valve was opened, the third harmonic (355 nm) of an Nd:YAG laser was weakly focused on the Ti disk with a spot size of ≤ 1 mm^2. The laser-ablated species containing metal ions and atoms traversed perpendicular 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 1 mm diameter 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 reflectron time-of-flight mass spectrometer, which was placed 10 cm downstream of the nozzle.

The positive ions were extracted by applying a high-voltage pulse in a single-stage extractor, and traveled along a field-free region of 1 m length. 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 by a 500 MHz digital oscilloscope coupled with a personal computer. Spectrophotometric grade C_2H_5OH (99.5%), CF_3CH_2OH (>99.5%), and CF_3CH_2OD (>99% 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.

2.2. Computations. The ground-state geometry of the $Ti^+-CF_3CH_2OH$ complexes and related reaction products were fully optimized at the B3LYP/6-311++G(d,p) level using the Gaussian 03W package, which includes Becke's three-parameter nonlocal hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr.[23] Two starting structures of Ti^+−2,2,2-trifluoroethanol complex were used in our calculations: one with the Ti^+ attached to the CF_3 end 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, $E(Ti^+-CF_3CH_2OH)$, and the total energies of Ti^+ and CF_3CH_2OH as separate entities, $E(Ti^+) + E(CF_3CH_2OH)$. To obtain the reaction energies for the $Ti^+ + CF_3CH_2OH$ system, the reaction products were also fully optimized at the same level. Zero-point-energy corrections were included when the reaction energies were calculated.

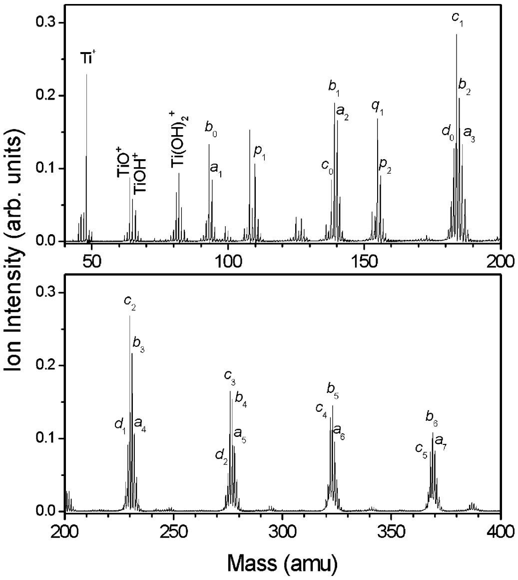


Figure 1. Mass spectrum of cluster ions produced by reactive collisions of laser-ablated Ti^+ and ethanol (EtOH) clusters seeded in 1.7 atm of Ar. The laser fluence was 42 mJ/cm^2. a_n, $Ti^+(EtOH)_n$; b_n, $Ti^+(OEt)(EtOH)_n$; c_n, $Ti^+(OEt)_2(EtOH)_n$; d_n, $Ti^+(OEt)_3(EtOH)_n$; p_n, $TiO^+(EtOH)_n$; q_n, $TiO^+(OEt)(EtOH)_n$.

3. Results and Discussion

3.1. Reactions of Ti^+ with Ethanol (EtOH) Clusters. Figure 1 shows a typical mass spectrum of the species present after the reaction of Ti^+ with C_2H_5OH clusters. The spectrum contains pentads of peaks corresponding to the Ti isotopes (^{46}Ti, 8.0%; ^{47}Ti, 7.3%; ^{48}Ti, 73.8%; ^{49}Ti, 5.5%; ^{50}Ti, 5.4%), with the relative intensities of these isotopomers reflecting their natural abundance. Unless otherwise noted, the results presented below refer to complexes involving the most abundant isotope. The prominent peaks in the mass spectrum consist of heterocluster ions with formulas $Ti^+(OEt)(EtOH)_n$, $Ti^+(OEt)_2(EtOH)_n$, and $Ti^+(OEt)_3(EtOH)_n$ (denoted b_n, c_n, and d_n), formed by the H-elimination reactions of the intact cluster ions $Ti^+(EtOH)_n$ (denoted a_n). These ethoxy-rich fragment ions are observed with up to 15 ethanol units in the present experiments. This result implies that the Ti^+ ion readily reacts with C_2H_5OH molecules solvated within heteroclusters.

The observation of peaks corresponding to the TiO^+ and $TiOH^+$ ions indicates that the reaction is initiated by insertion of Ti^+ into the C−O bond of an ethanol molecule. Product formation can be summarized in terms of the reactions below.

$$Ti^+(C_2H_5OH) \rightarrow [HO-Ti^+-C_2H_5]^{\ddagger} \rightarrow TiOH^+ + C_2H_5 \quad (3)$$

$$\rightarrow TiO^+ + C_2H_6 \quad (4)$$

Titanium has a lower ionization energy (IE) than ethanol (IE = 6.82 eV for Ti and 10.43 eV for C_2H_5OH). Hence, once the complex is formed, the positive charge in the heterocluster is expected to reside on the Ti. The enthalpy changes associated with reactions 3 and 4 are −16.7 and −63.1 kcal/mol, respectively,[17] indicating that these reactions are exothermic and thus energetically feasible. The formation of $TiOH^+$ (m/e = 65) from the [$HO-Ti^+-C_2H_5$] intermediate is plausible, because the estimated bond energy of $Ti^+-C_2H_5$ (57.5 kcal/mol), assuming that $D_0(Ti^+-C_2H_5) = D_0(Ti^+-CH_3)$,[24] is much lower than that of Ti^+-OH (111 kcal/mol).[25] The formation of metal hydroxide ions from methanol via elimination of CH_3 has been observed in systems involving other metal ions, including Mg^+, Fe^+, and Sr^+.[26−29] The observation of $Ti(OH)_2^+$ (m/e = 82) and $Ti(OH)_3^+$ (m/e = 99) product ions in the mass spectrum in Figure 1 can be interpreted as the outcome of sequential eliminations of C_2H_5 radicals within the heteroclusters. The formation of TiO^+ via reaction 4 is not surprising in the sense that Ti^+ bonds very strongly to oxygen atoms.[30] $TiO^+ + C_2H_6$ products arise from the [$HO-Ti^+-C_2H_5$] intermediate by hydrogen migration to form an $O-Ti^+-C_2H_5(H)$ transition state, followed by elimination of C_2H_6. A more detailed discussion of this reaction pathway is provided in section 3.3. Further, it is noted that peaks corresponding to $TiO^+(OEt)(EtOH)_n$ ions (labeled q_n) also emerge with negligible isotope contribution from the neighboring peaks. This result indicates that the TiO^+ ion within the $TiO^+(EtOH)_n$ (labeled p_n) cluster can undergo a subsequent H-elimination reaction with a solvating ethanol moiety.

As another major reaction channel, the Ti^+ ion can insert into the O−H bond of an ethanol molecule.

$$Ti^+(C_2H_5OH) \rightarrow [H-Ti^+-OC_2H_5]^{\ddagger} \rightarrow Ti^+(OC_2H_5) + H \tag{5}$$

The [$H-Ti^+-OC_2H_5$] intermediate formed by Ti^+ insertion can dissociate internally, with the $Ti^+(OC_2H_5)$ ion being produced via H elimination. In this reaction, the OC_2H_5 behaves more like a tightly bound group than a solvating ligand species. It has been found that the binding energies of Mg^+-OCH_3 (67.35 kcal/mol) and Co^+-OCH_3 (>69 kcal/mol) are much stronger than those of Mg^+-CH_3OH (37.7 kcal/mol) and Co^+-CH_3OH (35.28 kcal/mol).[24,30] Bonding in the $Ti^+-OC_2H_5$ ion is thus likely to resemble covalent bonding rather than an electrostatic interaction. The alternative internal reaction of the [$H-Ti^+-OC_2H_5$] intermediate—formation of the TiH^+ ion via $Ti^+-OC_2H_5$ bond rupture—is unfavorable due to the relatively low dissociation energy (54.2 kcal/mol) of the Ti−H bond.[24]

A surprising finding for $Ti^+(OEt)_m(EtOH)_n$ (m = 1−3) cluster ions is that H elimination in C_2H_5OH by the Ti^+ ion is possible for up to three ethanol molecules. This process proceeds via sequential H-elimination reactions:

$$[Ti^+(EtOH)_n]^{\ddagger} \rightarrow Ti^+(OEt)(EtOH)_{n-1} + H \tag{6}$$

$$\rightarrow Ti^+(OEt)_2(EtOH)_{n-2} + 2H \tag{7}$$

$$\rightarrow Ti^+(OEt)_3(EtOH)_{n-3} + 3H \tag{8}$$

In a recent study of the reactions of Ti^+ with EtOD clusters, we found that the dominant species are $Ti^+(OEt)(EtOD)_n$ and $Ti^+(OEt)_2(EtOD)_n$ series ions, which can only arise from cleavage of O−D bonds in the association complex $Ti^+(EtOD)_n$.[17] These results support our current conclusion that H eliminations due to the Ti^+ ion (reactions 7 and 8) occur from separate ethanol molecules. Within the stabilizing environs of a heterocluster, insertion of a $Ti^+(OEt)$ ion into a second ethanol molecule produces the $(EtO)Ti^+(H)(OC_2H_5)$ intermediate. This intermediate then dissociates internally and $Ti^+(OEt)_2$ ion is produced via H elimination. An abrupt decrease in the intensity of $Ti^+(OEt)_m(EtOH)_n$ cluster ions occurs for $m \geq 3$, which reflects the fact that the reactivity of the Ti^+ ion after $Ti^+(OEt)_2(EtOH)_n$ formation is strongly suppressed by the presence of the ethoxy ligands. A great reduction in the reactivity of Ti^+ due to the steric hindrance of the alkyl radical is also confirmed from the intracluster reactions of Ti^+ ion with alcohol compounds containing different alkyl groups.[16,17]

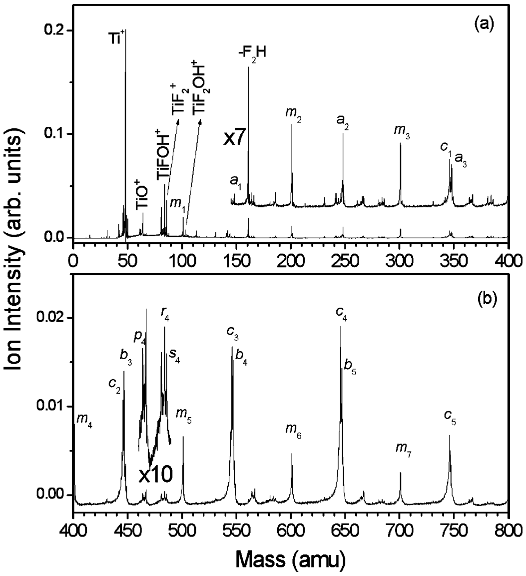


Figure 2. Mass spectrum of ions produced by reactions of Ti^+ with 2,2,2-trifluoroethanol (TFE) clusters. a_n, $Ti^+(TFE)_n$; b_n, $Ti^+(OCH_2CF_3)(TFE)_n$; c_n, $Ti^+(OCH_2CF_3)_2(TFE)_n$; m_n, $(TFE)_nH^+$; p_n, $TiO^+(TFE)_n$; r_n, $TiFOH^+(TFE)_n$; s_n, $TiF_2^+(TFE)_n$.

3.2. Ti^+ Reactions with 2,2,2-Trifluoroethanol Clusters. 2,2,2-Trifluoroethanol (CF_3CH_2OH; TFE) is a particularly interesting molecule because it possesses two functional groups, namely trifluoromethyl and hydroxyl groups. The substitution of the methyl group in ethanol with the highly electronegative CF_3 group is expected to alter the reaction pathways, offering an opportunity to further investigate the chemical reactivity of Ti^+ in the sequential insertion reactions observed for ethanol. A typical mass spectrum of the products of the reaction between Ti^+ and TFE clusters is shown in Figure 2. $(TFE)_nH^+$ cluster ions (denoted m_n) can be attributed to the intracluster protonation of the parent $(TFE)_n^+$ ions formed in the region where the laser-ablated plume and supersonic TFE cluster beam intersect. The peak at m/e = 161 can be assigned to the fragment ion formed by the loss of F_2H from the ionized TFE dimer. In the low mass region (Figure 2a), the reaction products consist of TiO^+ (m/e = 64), $TiFOH^+$ (m/e = 84), TiF_2^+ (m/e = 86), and TiF_2OH^+ (m/e = 103) produced by ion−molecule reactions of Ti^+ and TFE. These fragment ions are attributed to the following reactions.

$$Ti^+ + CF_3CH_2OH \rightarrow TiO^+ + CH_3CF_3 \tag{9}$$

$$\rightarrow TiFOH^+ + CH_2CF_2 \tag{10}$$

$$\rightarrow TiF_2^+ + CFCH_2OH \tag{11}$$

$$\rightarrow TiF_2OH^+ + CH_2CF \tag{12}$$

Unlike the $Ti^+ + C_2H_5OH$ system, in which $TiOH^+$ ions are generated by insertion of Ti^+ ions into the C−O bonds of C_2H_5OH molecules, the $TiOH^+$ ion is not observed among the products of the reaction of Ti^+ and TFE. This implies that rupturing the Ti^+-C bond of the [$HO-Ti^+-CH_2CF_3$] intermediate in the reaction of $Ti^+ + CF_3CH_2OH$ is less efficient than other product channels, presumably due to the different geometry of $[Ti^+\cdots CF_3CH_2OH]$ complex compared to that of $[Ti^+\cdots C_2H_5OH]$ complex. Very recently, Yang et al. reported that the Mg^+−TFE complex has a five-membered-ring structure, in which Mg^+ attaches to both the O atom and one of the three F atoms of TFE.[31] Another example is the reactions of $Fe^+ + ClCH_2CH_2Br$ and $Co^+ + ClCH_2CH_2OH$, 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.[32] Similarly, the observation that $TiFOH^+$ ion is formed in substantial quantities in the reaction of Ti^+ with CF_3CH_2OH strongly suggests that the reaction proceeds via a five-membered Ti^+(TFE) complex. We discuss this issue further in section 3.3. The observation in the mass spectrum of minor signals corresponding to $TiO^+(TFE)_n$ (p_n series), $TiFOH^+(TFE)_n$ (r_n series), and $TiF_2{}^+(TFE)_n$ (s_n series) cluster ions, however, demonstrates that reactions 9−11 are less favorable within the large heteroclusters. The mass spectrum in the high mass region (Figure 2b) consists of a major sequence of heterocluster ions of formula $Ti^+(OCH_2CF_3)(TFE)_n$ and $Ti^+(OCH_2CF_3)_2(TFE)_n$ (denoted b_n and c_n). Similar to the reactions between Ti^+ and C_2H_5OH clusters, the predominant reaction pathway is characterized by sequential insertions of Ti^+ ion into the O−H bond of TFE molecules within the parent $Ti^+(TFE)_n$ (a_n series) clusters, followed by H eliminations. These findings thus indicate that, as far as the intracluster reaction of Ti^+ with ethanol clusters is concerned, the dominant reaction pathway is not affected by replacing the H atoms on the CH_3 group of ethanol with F atoms.

It might be argued that successive H-elimination reactions via C−H bond insertion occur on a single TFE molecule. Unfortunately, the products resulting from H-elimination reactions of this type, $Ti^+(CF_3CHOH)(TFE)_n$ and $Ti^+(CF_3COH)(TFE)_n$, are indistinguishable from the O−H insertion products, $Ti^+(OCH_2CF_3)(TFE)_n$ and $Ti^+(OCH_2CF_3)_2(TFE)_{n-1}$, respectively, because they have identical masses. The results of isotope substitution experiments using deuterated TFE (*d*-TFE, CF_3CH_2OD) provide firmer evidence of the origin of H elimination within $Ti^+(TFE)_n$ heteroclusters. Specifically, by scrutinizing the mass spectrum of the products of the reactions of Ti^+ with $(d\text{-TFE})_n$, we can determine whether the peaks appearing at multiple mass units lighter than the parent cluster ion are from the loss of multiple H atoms from the CH_2 group or from sequential D eliminations of OD groups within the heteroclusters. The mass spectrum for the reactions of Ti^+ with *d*-TFE clusters is shown in Figure 3. In the mass spectrum, the dominant species consist of $Ti^+(OCH_2CF_3)(d\text{-TFE})_n$ (b_n series) and $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ (c_n series) ions, which can only arise from O−D cleavages in the association complex $Ti^+(d\text{-TFE})_n$ (a_n series).

$$[Ti^+(d\text{-TFE})_n]^\ddagger \rightarrow Ti^+(OCH_2CF_3)(d\text{-TFE})_{n-1} + D \qquad (13)$$

$$\rightarrow Ti^+(OCH_2CF_3)_2(d\text{-TFE})_{n-2} + 2D \qquad (14)$$

This result is in good agreement with the data of Lu and Yang,[33] who claimed that the hydrogen atom elimination channel of Mg^+ with methanol clusters leads to product ions with apparent stoichiometry $MgOCH_3{}^+(CH_3OH)_n$. In addition, the formation of $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n{}^+$ ions also supports our previous conclusion that H elimination due to the Ti^+ ion occurs in separate ethanol molecules.

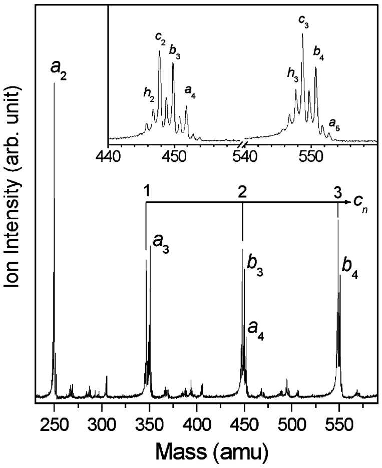


Figure 3. Mass spectrum of ions produced by reactions of Ti^+ with CF_3CH_2OD clusters. a_n, $Ti^+(CF_3CH_2OD)_n$; b_n, $Ti^+(OCH_2CF_3)(CF_3CH_2OD)_n$; c_n, $Ti^+(OCH_2CF_3)_2(CF_3CH_2OD)_n$; h_n, $Ti^+(OCH_2CF_3)_2(CF_3CHOD)(CF_3CH_2OD)_n$.

The isotope-labeling experiments provide additional evidence that is important for understanding H elimination within the heteroclusters. As can be seen from the inset of Figure 3, the h_n series of $Ti^+(OCH_2CF_3)_2(CF_3CHOD)(d\text{-TFE})_n$ ion signals are more prominent than would be expected. Although ${}^{48}Ti^+(OCH_2CF_3)_2(CF_3CHOD)(d\text{-TFE})_{n-1}$ ions are isobaric with the ${}^{47}Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ isotopomers of the c_n series, the apparent intensities of the h_n clusters are larger than would be predicted on the basis of natural isotopic abundances of titanium, a feature that becomes increasingly clear as the cluster size increases. This is because the loss of a H atom from $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ ion via C−H bond cleavage in a solvating molecule creates an h_n product.

$$Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n \rightarrow Ti^+(OCH_2CF_3)_2(CF_3CHOD)(d\text{-TFE})_{n-1} + H \qquad (15)$$

The observation of the h_n series implies that the $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ ions formed in the intracluster ion−molecule reactions can undergo a subsequent H-elimination reaction with CF_3CH_2OD within the clusters. This situation stands in contrast to the findings of our recent studies on the intracluster ion−molecule reactions of Ti^+ with CH_3OD clusters, in which sequential D eliminations via O−D bond breaking is the predominant reaction pathway for the formation of $Ti^+(OCH_3)_m(CH_3OD)_n$ ions ($m = 1-3$), and H elimination from the C−H bond of the methyl radical is hardly observed.[16] Taken together, these results suggest that increasing the chain length of the alkyl radical facilitates C−H bond cleavage in the heteroclusters.

To further investigate the competition between H elimination and D elimination, we examined the general trends in the size distribution of cluster ions. Figure 4 shows a plot of the intensities of the $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ (c_n series) and $Ti^+(OCH_2CF_3)_2(CF_3CHOD)(d\text{-TFE})_n$ (h_n series) ions, and their intensity ratios, h_n/c_n, as a function of the number of solvating *d*-TFE molecules within the heteroclusters. The increasing tendency of the h_n/c_n ratio with cluster size is suggestive of effective C−H bond cleavage via a Ti^+ insertion reaction after the $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ ions have formed. This is consistent with the view that the probability of H elimination by C−H bond cleavage increases with cluster size. Another distinctive feature in the intensity distribution of the heterocluster ions is that the $Ti^+(OCH_2CF_3)_2(d\text{-TFE})_n$ and $Ti^+(OCH_2CF_3)_2(TFE)_n$ ions (see also Figure 3) exhibit a local maximum at $n = 4$. This finding is independent of the stagnation pressure and laser fluence (i.e., it is independent of the cluster distribution produced

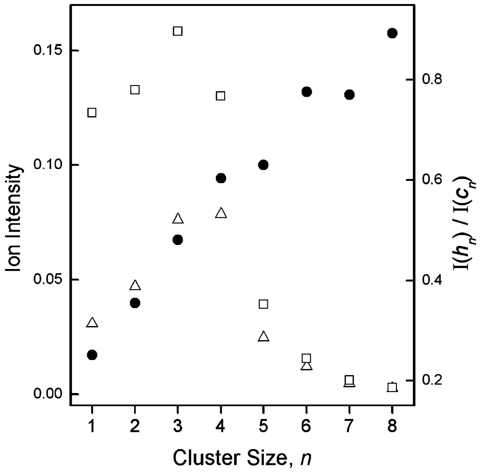


Figure 4. Intensity distribution of $c_n \equiv Ti^+(OCH_2CF_3)_2(CF_3CH_2OD)_n$ (□) and $h_n \equiv Ti^+(OCH_2CF_3)_2(CF_3CHOD)(CF_3CH_2OD)_n$ (△), and ion abundance ratio of h_n/c_n (●) as a function of number of CF_3CH_2OD molecules, *n*.

by reactive collisions), indicating that the $Ti^+(OCH_2CF_3)_2$(TFE or *d*-TFE$)_4$ ion has a particularly stable geometry in the solvating environment. Although detailed structural information is not yet available for $Ti^+(TFE)_n$ cluster ions, the current observation is consistent with the finding of El-Shall and co-workers[15] that the $Ti^+(OCH_2CF_3)_2(TFE)_4$ ion can be regarded as having an octahedral structure involving a core Ti^{3+} ion with two covalently bonded $OCH_2CF_3^-$ ligands.

3.3. Reaction Mechanism and Energetics. The results presented above indicate that Ti^+ is highly reactive toward TFE, with the involvement of insertion and elimination mechanisms, and that these reactions generate TiO^+, $TiFOH^+$, TiF_2^+, $TiOCH_2CF_3^+$, and their heterocluster ions. To interpret the reaction mechanism, we calculated the ground-state structures and absolute energies of the Ti^+-TFE complexes. At long range, the interaction between Ti^+ and CF_3CH_2OH species can be considered an ion−dipole attraction. Thus, the $Ti^+-CF_3CH_2OH$ complex is presumed to correspond to a minimum in the potential energy surface. The binding energy of CF_3CH_2OH to Ti^+ has not been measured or calculated to the best of our knowledge. 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.

The optimized structures of a CF_3CH_2OH molecule and two isomers of the $Ti^+-CF_3CH_2OH$ complex (referred to as I and II) are depicted in Figure 5, and their values for various parameters, including the total energy, bond lengths, bond angles, and atomic charges, are listed in Table 1. Complex I represents the case in which the Ti^+ ion attaches to two F atoms of the CF_3 group, leading to the formation of TiF_2^+ via C−F bond activation. When the Ti^+ ion approaches the TFE from the CF_3 group end, the molecule undergoes a significant structural change. For example, the three C−F bonds are almost equivalent in a free molecule, with bond lengths of 1.343−1.358 Å, whereas in complex I, the two C−F bonds adjacent to the Ti^+ are stretched to 1.399−1.404 Å and the other C−F bond shrinks to 1.309 Å. In addition, the bond angle $-F^2C^1F^3$ is 107.4° for the free molecule but 100.9° for the complex. The other bond lengths and angles, however, are almost the same in the free molecule and complex.

Complex II corresponds to the case in which Ti^+ interacts with both the O atom and one of the three F atoms of TFE, forming a complex containing a five-membered ring. This structure is similar to the intermediates of the $Mg^+ + o\text{-}C_6H_4F_2$, $Mg^+ + CF_3CH_2OH$, $Fe^+ + BrCH_2CH_2Cl$, and $Co^+ + ClCH_2CH_2OH$ reactions.[31,32,34] On going from the free TFE to complex II, the C^2-O and C^1-F^1 bonds are lengthened by 0.04−0.09 Å; thus it is likely that this bond weakening caused by Ti^+ insertion to form the complex ultimately leads to the rupture of these bonds. As such, the ground-state structure of TFE is changed only mildly when both the O atom and one of the F atoms are coordinated to Ti^+ to form a five-membered-ring complex. Note that structure II is more stable than structure I by 22.5 kcal/mol, suggesting that complex II is the more favorable of the two structures in the experiments carried out in the present work. The linkage of Ti^+ to O and F in complex II is consistent with our observation that the insertion reactions of Ti^+ ion into the C−F, C−O, and O−H bonds lead to the facile production of TiF_2^+, TiO^+, $TiFOH^+$, and $Ti^+(OCH_2CF_3)(TFE)_n$ ions. Moreover, since the Ti^+ ion in the complex is closer to the O atom (2.196 Å) than the F atom (2.248 Å), the C−O and O−H bonds appear to be easier to rupture than the C−F bond. The greater stability of complex II compared to complex I is also indicated by the less positive atomic charge of Ti^+ in complex II (+0.738) than in complex I (+0.750), which can be attributed to electron donation from the oxygen atom in the OH group.

The observed reaction pathways of $Ti^+\cdots CF_3CH_2OH$ (complex II) are summarized in Scheme 1 along with the calculated reaction energies. As can be seen from Scheme 1, the ion−molecule reactions leading to the formation of TiF_2^+, TiO^+, and $TiFOH^+$ ions are highly exothermic, indicating that they are energetically feasible reactions, as discussed above. It is noteworthy that the $Ti^+OCH_2CF_3 + H$ formation channel is clearly observed within the heteroclusters in spite of its small endothermicity. The ion−molecule reactions of Ti^+ with TFE can be divided into three categories: (i) C−O bond activation (reactions 9 and 10); (ii) C−F bond activation (reaction 11); (iii) O−H bond activation (reaction 13). Ti^+ insertion into the C−O bond of a CF_3CH_2OH molecule can lead to a $[HO-Ti^+-CH_2CF_3]$ intermediate. This intermediate could decompose to form $TiOH^+ + CH_2CF_3$ by simple bond fission of the Ti^+-C bond; however, our observation of a negligible signal corresponding to $TiOH^+$ in the mass spectra indicates that the reaction pathway involving Ti^+-C bond cleavage is less efficient than other reactions. Alternatively, the $[HO-Ti^+-CH_2CF_3]$ intermediate could undergo α-H atom transfer from the OH group to the Ti^+ ion, followed by CH_3CF_3 elimination, to produce TiO^+. This mechanism is analogous to the $Ti^+ + H_2O \rightarrow TiO^+ + H_2$ reaction, in which the dehydrogenation channel proceeds from a $[H-Ti^+-OH]$ intermediate by a H migration from O to form $[H_2-Ti^+-O]$ because Ti^+ has three valence electrons.[13] Last, the $[HO-Ti^+-CH_2CF_3]$ intermediate could produce $TiFOH^+$ followed by transfer of a F atom and elimination of CH_2CF_2. 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 due to their high exothermicity (−59.8 and −86.3 kcal/mol, respectively).

In addition to activating the C−O bond, the Ti^+ ion can also activate the C−F bond of a CF_3CH_2OH molecule to form the $[F-Ti^+-CF_2CH_2OH]$ intermediate. TiF^+ and $TiCF_2CH_2OH^+$ ions are expected to be produced via Ti^+-C and Ti^+-F bond dissociations, respectively. However, the absence of these product ions in the mass spectra indicates that simple bond fission of Ti^+-C or Ti^+-F does not take place. Nevertheless, our observation of TiF_2^+ among the products in the mass

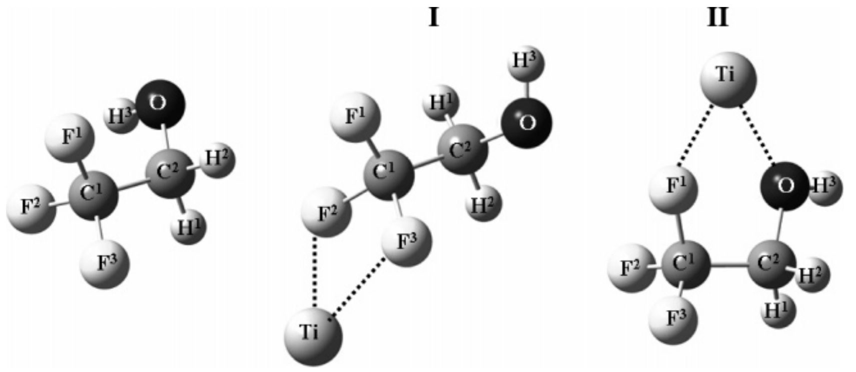


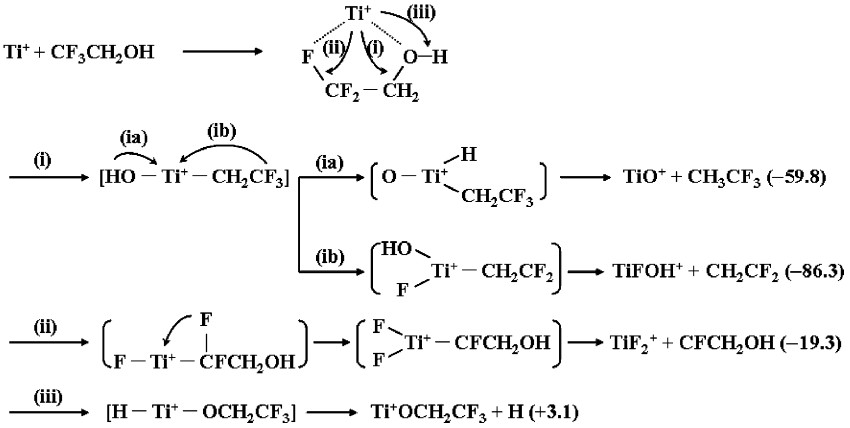
Figure 5. Optimized ground-state structures for a CF_3CH_2OH molecule and two possible Ti^+−2,2,2-trifluoroethanol complexes calculated at the B3LYP/6-311++G(d,p) level. Selected bond lengths in angstroms.

TABLE 1: Summary of B3LYP/6-311++G(d,p) Calculations for a CF_3CH_2OH Molecule and the Two Possible Ti^+−2,2,2-Trifluoroethanol Complexes

	bond lengths (Å)		bond angles (deg)		atomic charges (bond strength[a])	
CF_3CH_2OH	C^1-F^1: 1.343	C^2-H^1: 1.096	$F^1-C^1-F^2$: 107.2	C^1-C^2-O: 112.4	(C^1-F: 122.0)	
	C^1-F^2: 1.358	C^2-H^2: 1.090	$F^2-C^1-F^3$: 107.4	$H^1-C^2-H^2$: 108.8	(C^2-O: 93.4)	
	C^1-F^3: 1.351	C^2-O: 1.407	$F^1-C^1-C^2$: 113.0	C^2-O-H^3: 109.2	($O-H^3$: 114.1)	
	C^1-C^2: 1.523	$O-H^3$: 0.964			(C^2-H: 101.1)	
complex I (−302.056 572 09[b])	C^1-F^1: 1.309	C^2-H^2: 1.093	$F^1-C^1-F^2$: 107.6	H^2-C^2-O: 119.0	C^1: 0.160	Ti: 0.750
	C^1-F^2: 1.404	C^2-O: 1.396	$F^2-C^1-F^3$: 100.9	C^2-O-H^3: 111.1	C^2: −0.231	O: −0.248
	C^1-F^3: 1.399	$O-H^3$: 0.964	$F^1-C^1-C^2$: 115.6	C^1-F^2-Ti: 101.0	F^1: −0.008	H^1: 0.236
	C^1-C^2: 1.520	F^2-Ti: 2.361	C^1-C^2-O: 109.8	C^1-F^3-Ti: 102.7	F^2: −0.101	H^2: 0.227
	C^2-H^1: 1.095	F^3-Ti: 2.326	H^1-C^2-O: 114.6	F^1-Ti-F^2: 54.9	F^3: −0.081	H^3: 0.295
complex II (−1302.092 412 06[b])	C^1-F^1: 1.434	C^2-H^2: 1.091	$F^2-C^1-F^3$: 110.6	C^2-O-H^3: 111.1	C^1: 0.324	Ti: 0.738
	C^1-F^2: 1.322	C^2-O: 1.447	$F^2-C^1-F^1$: 105.3	C^1-F^1-Ti: 118.7	C^2: −0.400	O: −0.358
	C^1-F^3: 1.312	$O-H^3$: 0.966	$F^1-C^1-C^2$: 106.9	C^2-O-Ti: 121.2	F^1: −0.135	H^1: 0.257
	C^1-C^2: 1.521	F^1-Ti: 2.248	C^1-C^2-O: 106.4	F^1-Ti-O: 70.2	F^2: −0.043	H^2: 0.287
	C^2-H^1: 1.091	$O-Ti$: 2.196	$H^1-C^2-H^2$: 110.7		F^3: −0.026	H^3: 0.355

[a] Units are in kcal/mol. [b] Absolute energies in hartrees.

SCHEME 1: Summary of Observed Reaction Pathways of $Ti^+\cdots CF_3CH_2OH$ (Complex II) along with Calculated Reaction Energies (kcal/mol)



spectrum strongly suggests that F-atom transfer to form $[F_2-Ti^+-CFCH_2OH]$ plays a significant role. Finally, as a major reaction channel of $Ti^+(CF_3CH_2OH)_n$ heterocluster ions, the Ti^+ ion can insert into the O−H bond of a CF_3CH_2OH molecule. Because $Ti^+(OCH_2CF_3)(CF_3CH_2OH)_n$ and $Ti^+(OCH_2CF_3)_2(CF_3CH_2OH)_n$ ions are the predominant products observed in the present experiments, it is likely that insertion of Ti^+ into the O−H bond to form the $[H-Ti^+-OCH_2CF_3]$ intermediate is the most favored reaction channel among the three insertion routes (i.e., C−F, C−O, and O−H bonds). The dominance of the $Ti^+-OCH_2CF_3 + H$ product channel over the $Ti^+-H + OCH_2CF_3$ channel can be rationalized on the basis that the $Ti^+-OCH_2CF_3$ bond is stronger than the Ti^+-H bond. Qualitatively, the exit channel of $Ti^+OCH_2CF_3 + H$ formation (+3.1 kcal/mol) has the highest energy among the reaction products. By considering the strengths of the bonds in TFE (listed in Table 2), the calculated C−O bond activation (93.46 kcal/mol) is energetically favored over activations of the O−H (114.19 kcal/mol) and C−F (122.08 kcal/mol) bonds. However, despite the large O−H bond dissociation energy, this H elimination is observed to predominate in the heterocluster reactions. One

TABLE 2: Bond Dissociation Energy (BDE) Values (kcal/mol) of 2,2,2-Trifluoroethanol

bond	BDE
C−C	91.45
C−O	93.46
C−H	101.18
C−F	112.08
O−H	114.19

possible rationale for this result is that the breakage of the O−H bond in CF_3CH_2OH is compensated for by the formation of a strong $Ti^+-OCH_2CF_3$ bond and is further stabilized by the solvating molecules.

4. Conclusions

In the present study we investigated intracluster ion−molecule reactions within mixed $Ti^+(ROH)_n$ heterocluster ions ($R = C_2H_5$, CF_3CH_2) using a combination of laser ablation and supersonic beam expansion. The primary reactions produce a major sequence of $Ti^+(OR)_m(ROH)_n$ ions ($m = 1, 2$), which is attributed to sequential insertions of Ti^+ into the O−H bond of ethanol or TFE followed by H eliminations. The observation of $TiOH^+$ and TiO^+ ions among the reaction products of the reactions of Ti^+ with ethanol is understood on the basis of a C−O insertion reaction followed by C_2H_5 and C_2H_6 fragmentations, respectively. Substitution of the CH_3 group in ethanol with the more electronegative CF_3 group alters the reaction pathways such that $TiFOH^+$ and TiF_2^+ ions are produced in the ion−molecule reactions due to the distinct $Ti^+\cdots CF_3CH_2OH$ geometry. In addition, the observation of $Ti^+(OCH_2CF_3)_2(CF_3CHOD)(CF_3CH_2OD)_n$ ions in the isotope-labeling experiment is interpreted as indicating the occurrence of H elimination by C−H bond cleavage, 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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