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Intracluster ion–molecule reactions of Ti^+ with ethanol and *t*-butanol clusters

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Abstract

A laser ablation-molecular beam/reflectron time-of-flight mass spectrometric technique was used to investigate the ion–molecule reactions that proceed within $Ti^+(ROH)_n$ ($R = C_2H_5$, $(CH_3)_3C$) heterocluster ions. The mass spectra exhibit a major sequence of cluster ions with the formula $Ti^+(OR)_m(ROH)_n$ ($m = 1$–3); these cluster ions are attributed to the H elimination reactions produced by Ti^+ ions within the heteroclusters. The results also indicate that consecutive H eliminations by the Ti^+ ion can occur for up to three alcohol molecules. Isotope-labeling experiments suggest that H elimination is the dominant reaction pathway for O–H bond cleavage in Ti^+–alcohol heteroclusters. The $TiOH^+$ and TiO^+ ions observed in the mass spectra are interpreted here as arising from the insertion of Ti^+ ions into C–O bonds, followed by alkyl radical and molecular eliminations respectively from [HO–Ti^+–R] intermediates. The experiments also show that the chemical reactivity of Ti^+–alcohol heterocluster ions is greatly influenced by cluster size and by the nature of the alkyl group of the alcohol molecule. The observed reaction energetics and formation mechanisms of the heterocluster ions are also discussed.

Keywords: Ion–molecule reaction; Titanium; Heterocluster

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1. Introduction

The chemical reactions induced by the interaction of transition metal ions with various molecules have been studied extensively in order to elucidate the catalytic activity of metal ions, which is important in a wide range of areas of chemistry, including heterogeneous and homogeneous catalysis, inorganic chemistry, and biochemical processes [1–6]. Mass spectrometric studies of gas-phase ion–molecule reactions have also provided information about the chemistry of bimolecular interactions between ions and neutral molecules in the absence of complicating solvent phenomena [7]. Such gas-phase studies have provided insights into the intrinsic chemical and physical properties of transition metal ions; these insights have enhanced our understanding of the behavior of transition metal ions in the condensed phase.

The reactions of Ti^+ ions with methanol have been investigated in a number of previous studies. Castleman and coworkers have reported insertion reactions of Ti^+ ions into the C–H, C–O, and O–H bonds of methanol, which produce TiO^+, $TiOH^+$, $Ti(CH_2O)^+$, and $Ti(CH_3O)^+$ as the primary reaction products [8].

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The ion–molecule reactions of Ti^+ with methanol clusters have been studied by Sato and coworkers using a laser ablation-molecular beam method [9]. They suggested that the elimination of hydrogen molecules from $Ti^+(CH_3OH)_n$ cluster ions to produce $Ti^+(CH_3OH)_{n-1}CH_2O$ fragment ions is the dominant process:

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

In a recent study of the reactions of laser-generated Ti^+ ions with methanol clusters, El-Shall and coworkers proposed that the majority of the Ti^+-containing ions belong to the sequence $TiO^+(CH_3OCH_3)(CH_3OH)_n$, which they attributed to the catalytic conversion of methanol dimer into dimethyl ether by TiO^+ [10].

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

The above studies raise the interesting question as to whether the Ti^+ ion is primarily inserted into the methanol molecule, followed by H elimination (reaction 1) or oxidized to form TiO^+ (reaction 2) within the heteroclusters.

We recently reported our findings on the intracluster ion–molecule reactions of the $Ti^+(CH_3OH)_n$ ion [11]. Consecutive insertions of a Ti^+ ion into the O–H bonds of methanol molecules within the heteroclusters were found to play an important role in the production of $Ti^+(OCH_3)_m(CH_3OH)_n$ ions ($m = 1$–3). Further quantitative investigations of these reaction products are required to elucidate the reaction mechanism. The study of the specific chemical dynamics of reactions within cluster ions also provides valuable information on changes in the reaction pathways with increasing cluster size, which reflect the transition from gas-phase to solution-phase reactions [12–15]. Apart from the numerous studies of the reactions of Ti^+ ion with small molecules, no detailed experimental information on the mechanism and energetics of the reactions of Ti^+ ions with ethanol and *t*-butanol is available in the literature.

In the present study, we investigated the reactivity of Ti^+ ions with respect to the breaking of the C–H, C–C, C–O, and O–H bonds of ethanol and *t*-butanol molecules. The principal aim of the present work is to develop a quantitative interpretation of the reaction mechanisms that give rise to the observed mass spectra. In order to probe the reactions of these Ti^+–alcohol clusters, we used a combination of laser ablation and supersonic gas expansion techniques. Experiments with partially deuterated alcohols were used to help elucidate the reaction mechanisms for precursor activation by Ti^+. The present results provide further details of the intracluster reactions in heterocluster systems as well as thermochemical data for the enthalpies of these reactions. This study of the reactivities of titanium–alcohol heteroclusters as a function of cluster size also adds to the understanding of the influence of solvation on reactions within clusters and of the nature of the H elimination reactions of the Ti^+ ion on a molecular level.

2. Experimental methods

Fig. 1 shows the experimental setup, including the laser ablation-molecular beam (LA-MB), reflectron time-of-flight mass spectrometer (RTOFMS) and the timing sequence of the ion-extraction scheme. A rotating titanium disk (99.999%, Goodfellow) is mounted 2 cm downstream from the exit of a pulsed valve (General Valve, series 9). Clusters are formed via the adiabatic expansion through a pulsed nozzle of a gas mixture of alcohol molecules seeded in argon with a backing pressure of ∼25 psi. After opening the solenoid valve (τ_{d1}), the laser beam of a third harmonic (355 nm) of an Nd:YAG laser is weakly focused on the sample disk with a spot size of $\leq 1\,mm^2$. The laser-vaporized species travel perpendicular to the supersonic jet stream to a point 1 cm from the ablation sample target, where they interact with the alcohol clusters. The ion-alcohol complexes are then skimmed by a skimmer of diameter 1 mm and cooled collisionally as they travel through the detection region. The distance between the nozzle

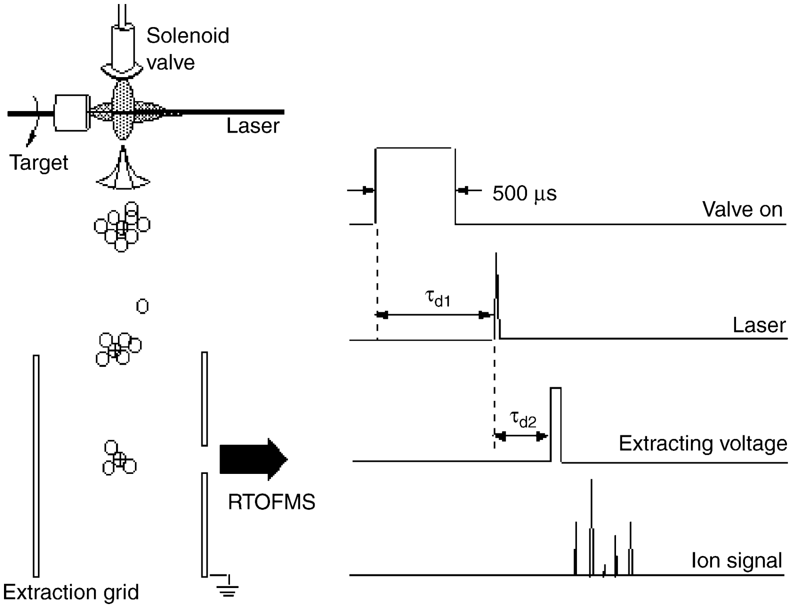

Fig. 1. Schematic diagram of the experimental setup for the coupling of a laser ablation-molecular beam source with a reflectron time-of-flight mass spectrometer.

and skimmer is 4 cm. The resulting pulsed beam enters the extraction region of the RTOFMS, which is placed 10 cm downstream of the nozzle. Under normal operating conditions, the pressures in the source and detection chambers were always below 3×10^{-5} and 5×10^{-7} Torr, respectively.

Following a delay (τ_{d2}) of typically 50–200 μs after the laser irradiation, the positive ions are accelerated vertically by a high voltage pulse (2200 V in amplitude and 1 μs in width) in a single stage extractor. 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 travel through a field-free region of length 1 m, which terminates at a double stage reflectron (R.M. Jordan Co.) located at the end of the flight tube. From the reflectron, the ions travel an additional 64 cm back to a chevron microchannel plate detector. The signal from the detector is sent to a digital storage oscilloscope (LeCroy LT322, 500 MHz) where in this study it was typically averaged over 1000 shots and further processed on a computer. Spectrophotometric grade C_2H_5OH (99.5%), C_2H_5OD (>99.5% D), and $(CH_3)_3COH$ (>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.

3. Results and discussion

3.1. The reactions of Ti^+ ions with ethanol clusters

Fig. 2 displays a typical mass spectrum resulting from the interaction of Ti^+ ions with ethanol (EtOH) clusters. The spectrum was obtained using a laser pulse energy of 42 mJ/cm^2 and an argon stagnation pressure of 1.7 atm. We observed pentads of peaks corresponding to the natural abundances of the isotopes of titanium (^{46}Ti, 8.0%; ^{47}Ti, 7.3%; ^{48}Ti, 73.8%; ^{49}Ti, 5.5%; ^{50}Ti, 5.4%). The peak $m/e = 45$ corresponds to the CH_3CHOH^+ ion, which is one of the major fragments observed in the mass spectrum of C_2H_5OH. The

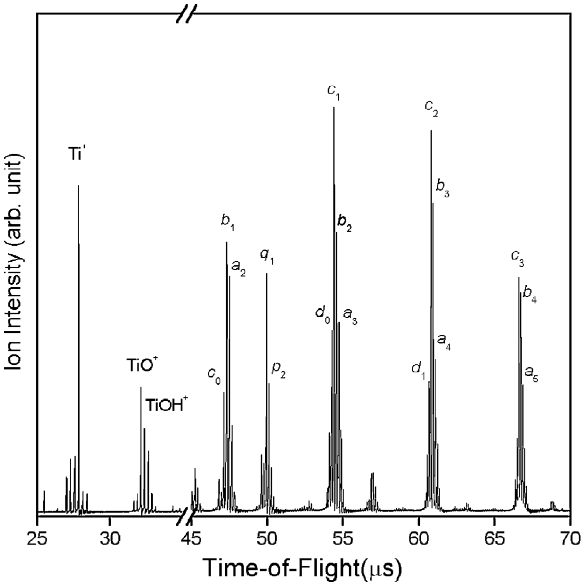

Fig. 2. Time-of-flight mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti^+ and ethanol (EtOH) clusters seeded in 1.7 atm Ar. The laser fluence is 42 mJ/cm^2. a_n: $Ti^+(EtOH)_n$; b_n: $Ti^+(OEt)(EtOH)_n$; c_n: $Ti^+(OEt)_2(EtOH)_n$; d_n: $Ti^+(OEt)_3(EtOH)_n$; p_n: $TiO^+(EtOH)_n$; q_n: $TiO^+(OEt)(EtOH)_n$.

Table 1
Energetics of possible reaction pathways of Ti^+ with C_2H_5OH[a]

Insertion site	Reaction products	Enthalpy (kcal/mol)
C–H bond	$Ti^+–H + C_2H_4OH$	41.8
	$Ti^+–C_2H_4OH + H$	38.5[b]
C–C bond	$Ti^+–CH_3 + CH_2OH$	29.4
C–O bond	$Ti^+–C_2H_5 + OH$	37.0
	$Ti^+–OH + C_2H_5$	–16.7
	$Ti^+–O + C_2H_6$	–63.1
O–H bond	$Ti^+–H + OC_2H_5$	50.5
	$Ti^+–OC_2H_5 + H$	–6.5[c]

[a] Reaction enthalpies are calculated from the thermochemical data provided in [18–20].

[b] The bond energy $D_0(Ti^+–C_2H_4OH)$ is assumed to equal $D_0(Ti^+–CH_3)$.

[c] The bond energy $D_0(Ti^+–OC_2H_5)$ is assumed to equal $D_0(Ti^+–OH)$.

characteristic abundance of the Ti isotopomers enables its complexes with ethanol clusters to be readily identified. Unless otherwise noted, the results presented below refer to complexes involving the most abundant isotope. The prominent peaks in the high mass region consist of heterocluster ions $Ti^+(OEt)_m(EtOH)_n$ ($m = 1–3$), formed from the H elimination reactions of the intact cluster ions $Ti^+(EtOH)_n$ (denoted a_n). These ethoxy-rich fragment ions were observed with up to 20 ethanol units in the present experiments. This result implies that the Ti^+ ion reacts with the C_2H_5OH molecules solvated within the heteroclusters. Titanium has a lower ionization potential than ethanol (IP values are 6.82 and 10.43 eV for Ti and C_2H_5OH, respectively). Hence, the positive charge in the heterocluster is expected to reside on Ti, once the complex is formed in the source. Evidence for this claim has been provided by several beam experiments on the formation of metal ion-organic molecules and metal ion-rare gas clusters [16,17].

The intracluster reaction of $Ti^+(EtOH)_n$ appears to have several possible reaction pathways since there are four types of chemical bond (C–H, C–C, C–O, and O–H) in an ethanol molecule that might permit the insertion of a Ti^+ ion. The enthalpies of the possible ion–molecule reactions, estimated from thermochemical data [18–20], are listed in Table 1. If C–H or C–C bond insertion takes place and the $[H–Ti^+–C_2H_4OH]$ or $[H_3C–Ti^+–CH_2OH]$ intermediate is formed, several product ions such as TiH^+, $TiC_2H_4OH^+$, $TiCH_3{}^+$, and $TiCH_2OH^+$ are expected to be produced through Ti–C and Ti–H bond dissociations. The absence of those product ions indicates that the C–H and C–C insertion processes do not occur within the heteroclusters, which is in reasonable agreement with the high endothermicity (ca. 30–40 kcal/mol) of those reactions. As the cluster size is increased, however, products of C–H insertions appear in the mass spectrum, as described later in this paper.

Another reaction channel is the C–O insertion reaction of the Ti^+ ion, which produces the $TiOH^+$ and TiO^+ ions that are observed in the mass spectrum. Product formation can be summarized in terms of the reactions below:

$$Ti^+(C_2H_5OH) \rightarrow [HO–Ti^+–C_2H_5]^\ddagger \rightarrow TiOH^+ + C_2H_5 \qquad (3)$$

$$\mathrm{Ti^+(C_2H_5OH)} \rightarrow [\mathrm{HO{-}Ti^+{-}C_2H_5}]^{\ddagger} \rightarrow \mathrm{TiO^+} + \mathrm{C_2H_6} \quad (4)$$

The enthalpy changes of reactions 3 and 4 are exothermic, −16.7 and −63.1 kcal/mol, respectively, suggesting that these reactions will appear as they become energetically feasible. The formation of $TiOH^+$ from the $[HO–Ti^+–C_2H_5]$ intermediate is plausible, because the bond energy of $Ti^+–C_2H_5$ (57.5 kcal/mol), estimated assuming that $D_0(Ti^+–C_2H_5)$ is equal to $D_0(Ti^+–CH_3)$ [20], is much lower than that of Ti^+–OH (111 kcal/mol) [21]. The formation of metal hydroxide ions from methanol, coinciding with the elimination of CH_3, has been observed in other metal ion systems, including Mg^+ [22], Fe^+ [23], and Sr^+ [24,25]. The formation of TiO^+ from reaction 4 is not surprising because Ti^+ ions form very strong bonds with oxygen atoms [26]. There are two mechanisms that are often considered for the formation of the TiO^+ ion, both arising from Ti^+ insertion into a C–O bond to form an $[HO–Ti^+–C_2H_5]$ intermediate. In the first mechanism, TiO^+ formation results from a four-centered elimination of C_2H_6 from this intermediate [27]. In the other mechanism, TiO^+ and C_2H_6 products arise from the intermediate by hydrogen migration to form an $O–Ti^+–C_2H_5(H)$ transition state, then by elimination of C_2H_6 [28]. However, the fact that only minor contributions from TiO^+ and $TiOH^+$ ions are evident in the mass spectrum demonstrates that the insertion reaction of Ti^+ into the C–O bond is less efficient than other pathways. Further, it is noted that peaks corresponding to $TiO^+(EtOH)_n$ and $TiO^+(OEt)(EtOH)_n$ ions (labeled as p_n and q_n, respectively) emerged. This result indicates that the TiO^+ ions formed from the ion–molecule reaction $Ti^+ + C_2H_5OH$ can undergo subsequent H elimination reactions with ethanol molecules within the clusters.

A major reaction channel is the insertion of a Ti^+ ion into the O–H bond of an ethanol molecule:

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

The $[H–Ti^+–OC_2H_5]$ intermediate dissociates and a $Ti^+(OC_2H_5)$ ion is produced via H elimination, with the OC_2H_5 in this species behaving more like a tightly bound group than a solvating ligand. It has been found that the binding energies of $Mg^+–OCH_3$ (67.35 kcal/mol) [26] and $Co^+–OCH_3$ (>69 kcal/mol) [20] are much stronger than those of $Mg^+–CH_3OH$ (37.7 kcal/mol) and $Co^+–CH_3OH$ (35.28 kcal/mol). Bonding in the $Ti^+–OC_2H_5$ ion is thus more likely to resemble covalent rather than electrostatic binding. The 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) [20] of the Ti^+–H bond.

The presence of the series of cluster ions $Ti^+(OEt)_m(EtOH)_n$ ($m = 1$–3) has the surprising implication that H elimination in C_2H_5OH by the Ti^+ ion is possible for up to three ethanol molecules. These ions probably arise from the sequential H elimination reactions:

$$[\mathrm{Ti^+(EtOH)}_n]^{\ddagger} \rightarrow \mathrm{Ti^+(OEt)} \times \mathrm{(EtOH)}_{n-1}(b_n \text{ series}) + \mathrm{H} \quad (6)$$

$$[\mathrm{Ti^+(EtOH)}_n]^{\ddagger} \rightarrow \mathrm{Ti^+(OEt)_2} \times \mathrm{(EtOH)}_{n-2}(c_n \text{ series}) + 2\mathrm{H} \quad (7)$$

$$[\mathrm{Ti^+(EtOH)}_n]^{\ddagger} \rightarrow \mathrm{Ti^+(OEt)_3} \times \mathrm{(EtOH)}_{n-3}(d_n \text{ series}) + 3\mathrm{H} \quad (8)$$

This scheme is in accord with the mass spectral data, which show peaks corresponding to the loss of one, two, or three mass units from the parent ion $Ti^+(EtOH)_n$. Within the stabilizing environs of a heterocluster, insertion of a Ti^+OEt ion into a second ethanol molecule, followed by H elimination, results in the formation of $Ti^+(OEt)_2$. There is room around the $Ti^+(OEt)_2$ ion for the addition of one more ethanol molecule, which produces the $(EtO)_2Ti^+(H)(OC_2H_5)$ intermediate. An abrupt decrease in the number of cluster ions with formula $Ti^+(OEt)_m(EtOH)_n$ occurs for $m \geq 4$, which suggests that the coordination of three OEt groups around a Ti^+ ion leads to a great reduction in the reactivity of Ti^+ with respect to breaking the O–H bond of additional ethanol molecules. The Ti^+ ion has three valence electrons, so this decrease is primarily attributable to the large binding

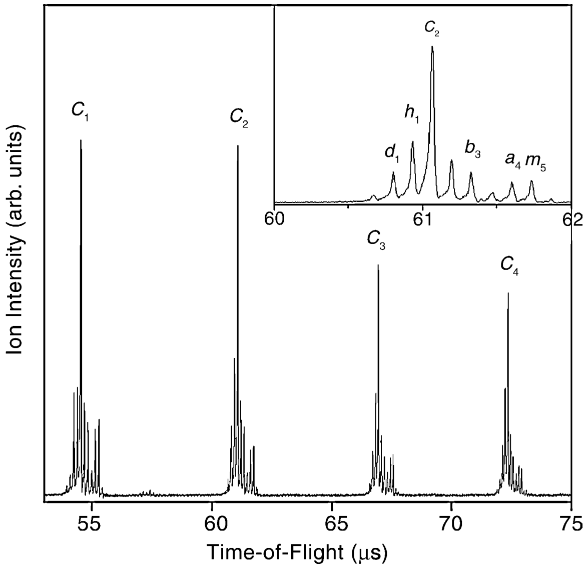

Fig. 3. Time-of-flight mass spectrum showing the ions produced by the reactions of Ti^+ with C_2H_5OD (EtOD) clusters. The laser fluence is 30 mJ/cm^2. a_n: $Ti^+(EtOD)_n$; b_n: $Ti^+(OEt)(EtOD)_n$; c_n: $Ti^+(OEt)_2(EtOD)_n$; d_n: $Ti^+(OEt)_3(EtOD)_n$; h_n: $Ti^+(OEt)_2(C_2H_4OD)(EtOD)_n$.

energy change that is caused when trivalent bond formation is completed by the three ligands with ethoxy groups. This interpretation seems reasonable since with four valence electrons, Ti is commonly observed in alkoxide compounds with a tetrahedral structure such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, $Ti(OC_3H_7)_4$, or Ti(O-*t*-Bu)$_4$.

It might be argued that successive H elimination reactions via C–H bond cleavage can occur on a single ethanol molecule, resulting in the products $Ti^+(C_2H_4O)(EtOH)_n$ and $Ti^+(C_2H_3O)(EtOH)_n$. Study of the reactions of Ti^+ with $(EtOD)_n$ enables us to determine if the peaks appearing at multiple mass units lighter than the peak of the parent cluster ion are from the loss of multiple H atoms from the C_2H_5 group or from sequential D eliminations of OD groups within the heteroclusters. The mass spectrum for the reactions of Ti^+ ions with $(EtOD)_n$ obtained with a laser pulse energy of 30 mJ/cm^2 and an argon stagnation pressure of 1.7 atm is presented in Fig. 3. Our data clearly show that the dominant species are $Ti^+(OEt)_2(EtOD)_n$ series ions, which can only arise from O–D cleavages from the association complex $Ti^+(EtOD)_n$. This result is in good agreement with the data of Lu and Yang [29], who claim 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 $Ti^+(OC_2H_5)_3(C_2H_5OD)_n{}^+$ ions also supports our previous conclusion that H elimination due to the Ti^+ ion occurs from separate ethanol molecules.

The isotope substitution experiments with deuterated ethanol provide additional evidence that is important for understanding H elimination within the heteroclusters. The observation of an h_n series corresponding to $Ti^+(OEt)_2(C_2H_4OD)(EtOD)_n$ ions, as shown in the inset of Fig. 3, is quite interesting. This series arises because the loss of an H atom from $Ti^+(OEt)_2(EtOD)_n$ ions via C–H bond cleavage in an ethanol molecule creates an h_n product. On the other hand, it was difficult to distinguish between the formation of $Ti^+(OEt)_3(EtOH)_n$ and $Ti^+(OEt)_2(C_2H_4OH)(EtOH)_n$ ions because they have identical masses when C_2H_5OH clusters are employed. Although $^{48}Ti^+(OEt)_2(C_2H_4OD)(EtOD)_{n-1}$ ions are isobaric with the $^{47}Ti^+(OEt)_2(EtOD)_n$ isotopomers of the c_n series, the apparent intensities of the h_n clusters are larger than predicted on the basis of natural isotopic abundances, which is clearly visible in Fig. 3 as the cluster size increases. This implies that C–H bond cleavage due to the Ti^+ insertion reaction competes with the O–D bond-breaking channel.

$$Ti^+(OEt)_2(EtOD)_n \rightarrow Ti^+(OEt)_3(EtOD)_{n-1} + D \qquad (9)$$

$$Ti^+(OEt)_2(EtOD)_n \rightarrow Ti^+(OEt)_2(C_2H_4OD) \times (EtOD)_{n-1} + H \qquad (10)$$

This situation contrasts with the results of our recent studies of the intracluster ion–molecule reactions of Ti^+ with CH_3OH and CH_3OD clusters, in which H elimination from methyl radicals is hardly detectable [11]. It seems that the increased chain length of the

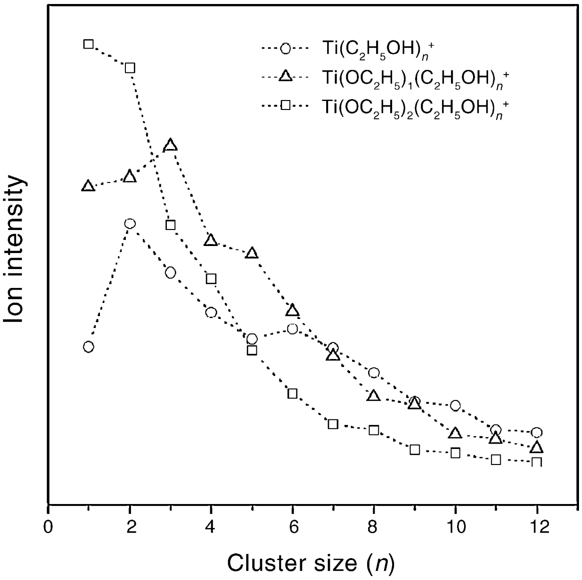

Fig. 4. Abundance distributions of $Ti^+(OEt)_m(EtOH)_n$ ions as a function of the number of ethanol molecules, n.

alkyl radical makes C–H bond cleavage in the clusters more likely.

To shed more light on the variation of the reactivity of the Ti^+ ion with cluster size, we investigated the general trends in the ion abundance distributions of the heteroclusters. Fig. 4 displays the intensity plot of the $Ti^+(OEt)_m(EtOH)_n$ ions ($m = 0$–2) as a function of cluster size n, obtained from the mass spectrum for the reaction of Ti^+ ions with $(EtOH)_n$ clusters. In the small cluster region $n \leq 4$, the intensity of the peaks corresponding to $Ti^+(EtOH)_n$ (a_n) ions is lower than those of the $Ti^+(OEt)(EtOH)_n$ (b_n) and $Ti^+(OEt)_2(EtOH)_n$ (c_n) cluster ions, presumably because of the reactive insertions of Ti^+ ions followed by H eliminations within the small heteroclusters. As the cluster size increases, however, the intensities of the peaks corresponding to $Ti^+(EtOH)_n$ ions become comparable with those of the H elimination products. This phenomenon, known as 'product switching', has also been observed in the reactions of alkaline-earth metal cations M (M = Mg^+, Ca^+, Sr^+, and Ba^+) with methanol clusters, where for $n \geq 15$ the species $M^+(CH_3OH)_n$ is dominant, with only very small quantities of the $M^+(OCH_3)(CH_3OH)_{n-1}$ series present [29]. In the large cluster region, the intensity of heterocluster series occurs in the order $a_n > b_n > c_n$ and this trend is maintained for all $n \geq 7$. These results show that the reactivity of the Ti^+ ion diminishes with increasing solvation by ethanol molecules. This apparent quenching of H elimination reactions is attributed to increased stabilization of the $Ti^+(EtOH)_n$ ions as the degree of solvation increases. In addition, it is believed that the presence of ethanol molecules around the metal ion produces an energy barrier in the reaction pathway for H elimination. Because the ease of hydrogen atom transport after O–H bond cleavage is greatly reduced within such a tightly packed solvent cage, the trapping probability of hydrogen atoms eliminated from C_2H_5OH molecules is expected to increase with increasing cluster size [26]. Thus H elimination reactions might be suppressed in sufficiently large clusters.

3.2. The reactions of Ti^+ ions with t-butanol clusters

The *t*-butyl group is a particularly interesting substituent, because of both its high intrinsic stability and its bulkiness. The substitution of the ethyl radical with the more bulky $(CH_3)_3C$ group is expected to alter the ion–molecule reaction pathways, offering an opportunity to investigate the chemical reactivity of Ti^+ with respect to the sequential insertion reactions. A typical TOF mass spectrum of the products of reaction between Ti^+ ions and *t*-butanol (*t*-BuOH) clusters is displayed in Fig. 5. It exhibits a major sequence of heterocluster ions with the formula $Ti^+(OBu)_2(BuOH)_n$ (denoted c_n). As for the reactions between Ti^+ ions and ethanol clusters, these heteroclusters are attributed to H elimination reactions within the parent $Ti^+(BuOH)_n{}^+$ ions. The pronounced formation of $Ti^+(OBu)_2(BuOH)_n$ ions can be interpreted as due to the extensive evaporation (i.e., boil-off) of weakly bound *t*-butanol molecules from the exterior of the cluster. This evaporation is a result of the excess energy available from the exothermicity of the intracluster ion–molecule reactions.

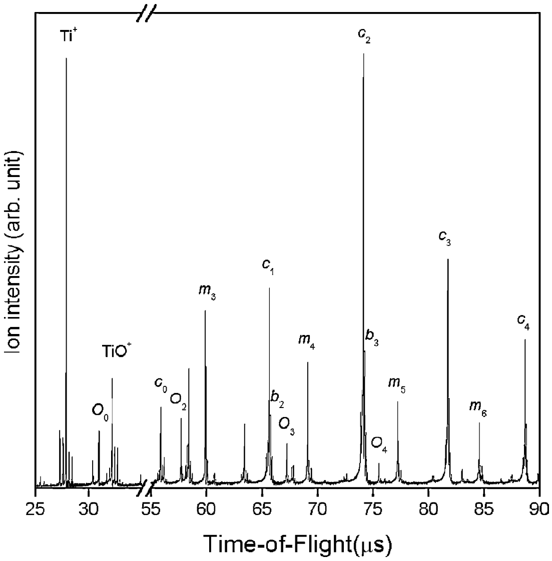

Fig. 5. Time-of-flight mass spectrum showing the ions produced by the reactions of Ti^+ with *t*-butanol (BuOH) clusters. b_n: $Ti^+(OBu)(BuOH)_n$; c_n: $Ti^+(OBu)_2(BuOH)_n$; m_n: $(BuOH)_nH^+$; o_n: $(CH_3)_2C{=}OH^+(BuOH)_n$.

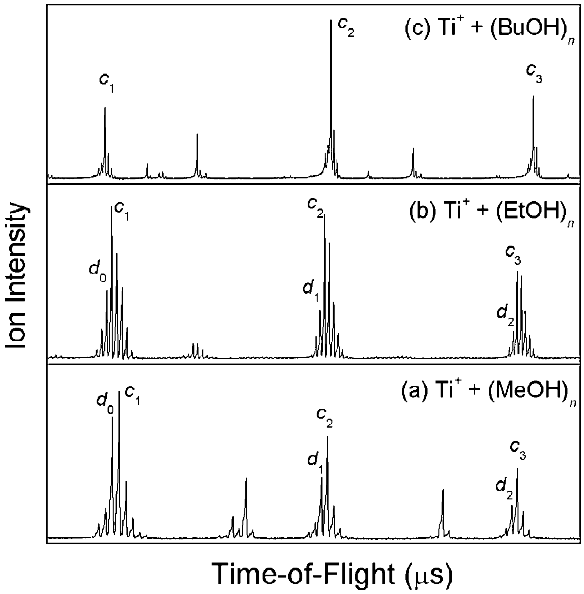

Fig. 6. Comparison of the time-of-flight mass spectra resulting from the reactions of Ti^+ ions with (a) methanol, (b) ethanol, and (c) *t*-butanol clusters.

Although of much lower intensity, the fragment ions o_n corresponding to $(CH_3)_2C{=}OH^+(BuOH)_n$, can be recognized in the mass spectrum. These ions might be produced by the $Ti^+ + (BuOH)_n \rightarrow Ti + (BuOH)_n^+$ charge transfer reaction and subsequent α-cleavage fragmentation of ionized *t*-butanol within the clusters, which is a characteristic reaction of tertiary alcohols. The absence of $TiOH^+$ ions is not surprising: the $(CH_3)_3C$ radical can easily accommodate the positive charge of a titanium ion in a $[(CH_3)_3C–Ti^+–OH]$ intermediate because the ionization energy of the $(CH_3)_3C$ radical (6.7 eV) [30] is almost identical with that of a Ti atom (6.82 eV). Thus Ti–C bond cleavage from the intermediate gives rise to the formation of stable $(CH_3)_3C^+$ ions and TiOH molecules, a reaction which is energetically more favorable than the formation of $TiOH^+$ ions and $(CH_3)_3C$ radicals.

To investigate the effect of the size of the alkyl radicals on the chemical reactivity of the heterocluster ions, the mass spectra produced by the reactions of Ti^+ ions with methanol, ethanol, and *t*-butanol clusters are compared in Fig. 6. Each spectrum shows peaks corresponding to $Ti^+(OR)_m(ROH)_n$ clusters ($3 \leq m+n \leq 5$). When Ti^+ ions react with methanol clusters (Fig. 6a), the H, 2H, and 3H elimination products are observed, with the 2H elimination process dominating. The relatively small methanol (MeOH) molecules solvating the Ti^+ ion have a higher chance of reacting with the Ti^+ ion, resulting in a greatly enhanced peak in the mass spectrum corresponding to $Ti^+(OMe)_3(MeOH)_n$ ions. In the case of the reactions of Ti^+ ions with ethanol clusters, however, the sequential reactions of Ti^+ ions with neutral ethanol molecules become progressively less favorable, because of the increased chain length of the alkyl radicals within the heteroclusters. The $Ti^+(OEt)_3(EtOH)_n$ ions (d_n series) are substantially decreased in abundance whereas the d_n series shows a considerable contribution compared with the c_n series in the methanol heteroclusters spectrum. This observation is easily explained by the steric effect of the alkyl radical. The ethyl radical possesses a longer alkyl chain than the methanol molecule, so the chemical reactivity of the Ti^+ ion after $Ti^+(OEt)_2(EtOH)_n$ formation is strongly

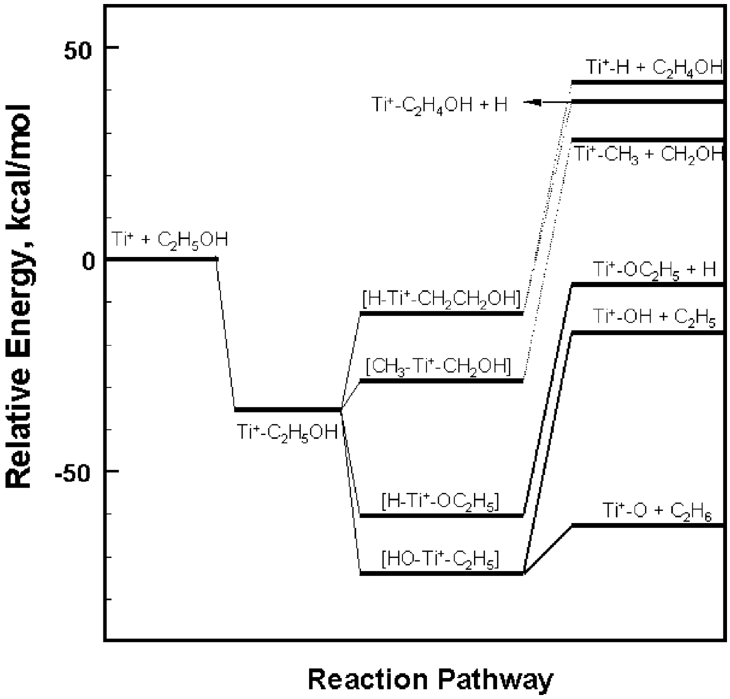

Fig. 7. Schematic energy diagram for the ion–molecule reactions of Ti^+ and C_2H_5OH.

suppressed by the two ethoxy ligands. The suggestion that Ti^+ reactivity is suppressed by the steric hindrance of the alkyl radical is also supported by the even lower intensity of the d_n series in the reactions of Ti^+ with *t*-butanol. The minor contribution of d_n ions compared to that in the case of $Ti^+ + (MeOH)_n$ indicates that the sequential insertion of $Ti^+(OBu)_2$ ions into additional *t*-butanol molecules is unfavorable due to the bulkiness of the two butoxy groups already bonded to the Ti^+ ion. Therefore, the present results strongly suggest that H elimination reactions within the clusters are highly dependent on the size of the alkyl radicals.

3.3. Reaction energetics

Fig. 7 shows a schematic energy diagram of the reaction pathways of $Ti^+ + C_2H_5OH$, which was constructed from the calculated thermochemical data. This diagram provides a useful guide to the reaction energetics of the heterocluster systems explored in the present work. The electronic state of the Ti^+ ion that correlates with the reaction products is the $a^4F(3d^24s)$ state, the lowest quartet state having an s electron [20]. Recent studies have shown that the reactions of metal ions with molecules are affected by the electronic state and kinetic energy of the metal ion [19,20,31]. While we cannot exclude all the possible reactions of electronically excited Ti^+ ions, we believe that the observed reaction patterns in the current experiments are mainly due to ground-state reactions. This is because the laser-ablated Ti^+ ions are likely to be efficiently quenched by their collision with the supersonic beam of C_2H_5OH/Ar. In addition, the failure to observe any reaction products from the endothermic reaction channels even at high laser fluence supports our hypothesis that Ti^+ ions in high-lying states make no appreciable contribution to the H, C_2H_5, and C_2H_6 elimination reactions.

The broad distribution of the kinetic energies of the laser-ablated Ti^+ ions may also influence the observed reaction patterns. Nevertheless, we have good reason to believe that the product ions observed in the present experiments are those resulting from Ti^+ ions with very low kinetic energy. One would expect that the kinetic energy of the Ti^+ ions would be greatly reduced by collisional quenching with the argon carrier gas, resulting in the production and detection of relatively stable clustered product ions. Much of the kinetic energy may also be dissipated by evaporation of solvent ethanol molecules from the clusters. This is consistent with the present observation that the chemical reactivity of the Ti^+ ion diminishes with increasing degree of C_2H_5OH solvation. Further, product ions formed from high kinetic energy Ti^+ ions will have a large momentum along the laser-ablation axis, and so cannot enter the ion extraction region of the TOF mass spectrometer. Thus the cluster ions sampled in the present experimental apparatus correspond to those originating preferentially from relatively low-energy Ti^+ ions.

As displayed in Fig. 7, it is noteworthy that the ion–molecule reactions leading to the formation of TiO^+, $TiOH^+$, and $Ti^+OC_2H_5$ ions are exothermic, indicating that these are the energetically feasible reactions, as discussed earlier. At long range the interaction between Ti^+ and C_2H_5OH species can be treated as an ion-dipole attraction. Thus, the Ti^+–C_2H_5OH complex is assumed to correspond to a local minimum in the potential energy. The binding energy between C_2H_5OH and 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 involving a direct linkage between the two. Comparison with the literature values for metal ion–molecules such as Ti^+–C_3H_6 (34.5 kcal/mol) [32], Ti^+–H_2O (36.9 kcal/mol) [33], Co^+–H_2O (37.1 kcal/mol) [34], Co^+–CH_3OD (35.3 kcal/mol) [35], and Mg^+–CH_3OH (37.7 kcal/mol) [26] allows us to obtain an approximate Ti^+–C_2H_5OH binding energy of 35 kcal/mol.

Insertion of Ti^+ ions into the C–H, C–C, C–O, and O–H bonds of an ethanol molecule can lead to four intermediates. The formation energies of [H–Ti^+–CH_2 CH_2OH], [CH_3–Ti^+–CH_2OH], [H–Ti^+–C_2H_5O], and [OH–Ti^+–C_2H_5] intermediates are estimated to be -11.9, -28.0, -60.8, and -74.2 kcal/mol, respectively, based on the bond additivity assumption that the bond energy $D_0(Ti^+–C_2H_4OH) \approx D_0(Ti^+–CH_3)$ and that $D_0(Ti^+–OC_2H_5) \approx D_0(Ti^+–OH)$. Although this assumption may not be quantitatively accurate, it is the only available means for estimating the energy of the four possible intermediates. The intermediate [H–Ti^+–CH_2CH_2OH] can decompose to form Ti^+–H + C_2H_4OH ($\Delta H_{rxn} = 41.8$ kcal/mol) or Ti^+–C_2H_4OH+H ($\Delta H_{rxn} = 38.5$ kcal/mol) by simple bond fissions of the Ti–C or Ti–H bonds, respectively. However, both product channels are thermodynamically unfavorable due to their high endothermicity, which is consistent with the present experiments. The formation of Ti^+–CH_3 or Ti^+–CH_2OH ions from the [CH_3–Ti^+–CH_2OH] intermediate followed by Ti–C bond breaking is also endothermic ($\Delta H_{rxn} = 29.4$ kcal/mol).

In addition to activation of the C–H and C–C bonds, the Ti^+ ion can insert into the O–H or C–O bonds of an ethanol molecule. Relative to the Ti^+–C_2H_5OH complex, the formation reactions of [H–Ti^+–OC_2H_5] and [HO–Ti^+–C_2H_5] intermediates are exothermic by 25.8 and 39.2 kcal/mol, respectively. The formation energies of these intermediates suggest that the O–H and C–O insertion reactions will appear as they become energetically feasible. Because Ti^+–OC_2H_5 is the predominant ionic product observed in the present experiments, it is likely that Ti^+ insertion into the O–H bond to form the [H–Ti^+–OC_2H_5] intermediate is the most favored reaction channel of the four possible routes. The dominance of the Ti^+–OC_2H_5 + H product channel over the Ti^+–H + OC_2H_5 channel can be rationalized on the basis that a Ti^+–OC_2H_5 bond is stronger than a Ti^+–H bond.

The eliminations of C_2H_5 and C_2H_6 from the [HO–Ti^+–C_2H_5] intermediate might occur efficiently because these channels are thermodynamically much more favorable. The overall reaction energies for Ti^+–OH + C_2H_5 and Ti^+–O + C_2H_6 product formation are -16.7 and -63.1 kcal/mol, respectively. However, the small contributions of the Ti^+–OH and Ti^+–O ions to the present mass spectrum suggests that there are considerable barriers between the

[HO–Ti$^+$–CH$_3$] intermediate and the eliminations of C_2H_5 and C_2H_6. In a crossed molecular beam study of the Ba + CH_3OH system, Davis et al. [36] reported that both ground (^{1}S) and excited (^{1}D) electronic state Ba produced $BaOCH_3$ almost exclusively, although the channel for production of BaOH is energetically more facile. They ascribed this remarkable selectivity to the potential energy barriers; the most likely pathway for the H elimination is a migration mechanism. Therefore, we attribute the difference in importance of the two intermediates, [H–Ti$^+$–OC$_2$H$_5$] and [HO–Ti$^+$–C$_2$H$_5$], to a difference in the activation barriers for the subsequent elimination, but complete understanding of these reactions awaits a further study.

4. Conclusion

Reactions that proceed within mixed titanium–ethanol and *t*-butanol heterocluster ions were studied using the laser ablation-molecular beam method. The interaction of Ti$^+$ ions with alcohol (ROH) clusters appears to have three open elimination channels: H, R, and RH eliminations, with H elimination being the dominant process. In studies of the origin of the hydrogen elimination, isotope-labeling experiments led us to conclude that insertions of Ti$^+$ ions into the O–H bonds of alcohol molecules within the heteroclusters play an important role in producing $Ti^+(OR)_m(ROH)_n$ ions. In addition, it was found that the Ti$^+$ ion can induce successive H eliminations from up to three alcohol molecules. This result is interpreted to be a consequence of consecutive insertion reactions of the Ti$^+$ ion within the heteroclusters, leading to the formation of $Ti^+(OR)_3(ROH)_n$ ions. The observation of TiOH$^+$ and TiO$^+$ ions is interpreted here on the basis of a C–O insertion reaction followed by fragmentation. It is also found that the sequential insertion of $Ti^+(OR)_2$ ion into additional ROH molecules is suppressed by the steric hindrance of the two alkoxy groups already bonded to the Ti$^+$ ion. The chemical reactivity of Ti$^+$ ions within the heteroclusters decreases with increasing cluster size. The reaction pathways and energetics of the proposed mechanisms have been presented.

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