Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 243 (2005) 97–104

www.elsevier.com/locate/ijms

Intracluster ion–molecule reactions of Ti^+ with ether clusters

Young-Mi Koo, Min-Kyung Kim, Kwang-Woo Jung*

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

Received 4 October 2004; accepted 27 December 2004
Available online 1 February 2005

Abstract

The intracluster ion–molecule reactions of $Ti^+(CH_3OR)_n$ ($R = CH_3$, n-C_3H_7, n-C_4H_9, t-C_4H_9) complexes produced by the mixing of laser-vaporized plasmas and pulsed supersonic beams were investigated using a reflectron time-of-flight mass spectrometer (RTOFMS). The reactions of Ti^+ with dimethyl ether clusters were found to be dominated by the CH_3 elimination reaction, which produces $Ti^+(OCH_3)_m(CH_3OCH_3)_n$ clusters ($m = 1$–3). The mass spectra resulting from the reactions of Ti^+ with the other ether clusters indicate the formation of major sequences of heterocluster ions with the formula $Ti^+(OCH_3)_x(OR)_y(CH_3OR)_n$, where $x = 1$–3 and $y = 0$–2. 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. The prevalence of radical elimination of longer alkyl groups rather than of CH_3 radicals suggests that R elimination from the $[CH_3O{-}Ti^+{-}R]$ intermediate is the preferred decomposition pathway after the selective insertion of a Ti^+ ion into the C─O bond of an OR group. Our results also indicate that consecutive insertions of a Ti^+ ion can occur for up to three precursor molecules. The experiments also show that the molecular eliminations of H_2 and alkanes, resulting from C─H and C─C bond insertion, respectively, play an increasingly important role as the size of the alkyl group (R) in the ether molecule increases. The reaction energetics and the formation mechanisms of the observed heterocluster ions are also discussed.

Keywords: Ion–molecule reaction; Titanium; Ether; Heterocluster

1. Introduction

The study of the chemistry of transition metal ions in the gas phase is a rapidly expanding field of research, since these ions play a critical role in a variety of chemistries ranging from industrial catalysis to biological activity. It is therefore important to understand the fundamental aspects of the intrinsic chemistry of these species. The highly reactive properties of transition metal ions in the gas phase have been demonstrated by several investigations into the reactions of gas-phase transition-metal ions with a variety of organic species using ion cyclotron resonance (ICR) spectroscopy [1,2] and ion beam techniques [3–8]. These gas-phase studies have provided insights into the intrinsic chemical and physical properties of transition metal ions that have enhanced our understanding of the behavior of transition metal ions in the condensed phase.

Studies of the reactions of Ti^+ with small alkane molecules have revealed that Ti^+ is very active in the breaking of C─H and C─C bonds, leading to the eliminations of H_2 and alkanes, respectively [9–12]. The alkanes were found to be cleaved by the metal ion via oxidative-addition reactions, which arise from either a C─H or C─C insertion [13]. In studies of the reactions of Ti^+ with water using the selected ion drift tube technique [11] and guided ion beam tandem mass spectrometry [14], it has been reported that the primary reaction channel proceeds via Ti^+ insertion into the O–H bond to form a $H{-}Ti^+{-}OH$ intermediate, which then loses H_2 to produce TiO^+. Another study of the gas-phase ion–molecule reactions of Ti^+ with a series of ketones, aldehydes, ethers, and esters has shown that Ti^+ extracts an oxygen atom from small carbonyl compounds and cyclic ethers to form TiO^+ [15]. However, the reactions of Ti^+ with organic molecules remain a

---

* Corresponding author. Tel.: +82 638506208; fax: +82 638414893.
E-mail address: kwjung@wonkwang.ac.kr (K.-W. Jung).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.12.032

subject of much debate; the unresolved issues include fundamental mechanistic concerns such as the relative reactivity of Ti^+ toward insertion and elimination reactions, and the structures surrounding this ion under solvation conditions.

Although the products of gas-phase ion–molecule reactions have been extensively investigated, few studies have examined the chemical reactions taking place within heterocluster ions. The product distribution of metal ion–solvent heteroclusters provides valuable information about the changes in the reaction pathways with increasing cluster size, which reflect the transition from gas-phase to solution-phase reactions [16–18]. Recently, our group reported the predominant H-eliminations in the reactions of Ti^+ with ROH ($R = CH_3$, C_2H_5, t-$(CH_3)_3C$) clusters, which produce $Ti^+(OR)_m(ROH)_n$ ($m = 1$–3) heteroclusters [19,20]. The primarily reaction channel proceeds via Ti^+ insertion into the O–H bond of alcohol molecule to form a [RO–Ti^+–H] intermediate, which then loses H atom. We also found that the consecutive H-eliminations by the Ti^+ ion can occur for up to three alcohol molecules within the heteroclusters. This reactivity of Ti^+ ion (i.e., bond-selective insertions and consecutive eliminations) is a unique property not found in other transition metal ions. 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 ether molecules is available in the literature.

In the present study, we investigated the reactivity of Ti^+ ions with respect to the breaking of the C–O, C–C, and C–H bonds in ether molecules within heterocluster ions. The principal aim of the present work is to develop a quantitative interpretation of the reaction mechanisms suggested by our observations. To probe the cluster reactivity, we examined the reactions in heteroclusters produced by laser ablation and supersonic gas expansion. Studying the variation of the reactivity of titanium–ether heteroclusters with alkyl radical size also adds to our understanding of the nature of the alkyl radical elimination reactions of the Ti^+ ion on a molecular level.

2. Experimental methods

The present experiments were performed using apparatus described elsewhere [21]. Briefly, the two-stage system is composed of differentially evacuated chambers, which contain a cluster beam source and a reflectron time-of-flight mass spectrometer (RTOFMS). The pressures of the source and TOFMS chambers were maintained at about 2×10^{-5} and 6×10^{-7} Torr, respectively during the measurements. Clusters of Ti^+ ions and ether molecules, $Ti^+(CH_3OR)_n$ ($R = CH_3$, n-C_3H_7, n-C_4H_9, t-C_4H_9), were produced by the combination of laser vaporization and pulsed supersonic expansion. The sample gas mixed with helium was expanded from a pulsed valve (General Valve, series 9, orifice diameter 0.8 mm) with a stagnation pressure of 1.5 atm. After opening the solenoid valve, the third harmonic output (355 nm) of an Nd:YAG laser was focused onto a rotating Ti target (Goodfellow, 99.999%) located 2 cm downstream from the nozzle. The laser-vaporized metal ions perpendicularly crossed the expansion stream 1 cm from the target, where they react with the neutral ether clusters formed in the pulsed jet. The resulting ion complexes were then introduced into the RTOFMS chamber after collimation with a conical skimmer (throat diameter of 1 mm) positioned 4 cm downstream from the nozzle.

Following a delay of typically 50–200 μs after the laser irradiation, the positive ions were extracted with a 2.2 keV pulsed electric field, applied to the repeller. The delay times between valve opening, laser firing, and the ion extraction pulse were optimized using a digital delay/pulse generator (Stanford Research, DG535). 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., D-850) 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 output signals from the detector were sent to a digital storage oscilloscope (LeCroy LT322, 500 MHz), where they were averaged over typically 1000 shots and further processed on a computer. Spectrophotometric grade CH_3OCH_3 (Aldrich, >99%), $CH_3OCH_2CH_2CH_3$ (TCI, >95%), $CH_3OCH_2CH_2CH_2CH_3$ (Aldrich, >99%), and $CH_3OC(CH_3)_3$ (Aldrich, >99.8%) 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 dimethyl ether clusters*

A typical TOF mass spectrum of the products of reaction between Ti^+ and dimethyl ether (DME, CH_3OCH_3) clusters is displayed in Fig. 1. The spectrum was obtained using a laser pulse energy of 24 mJ/cm^2 and an argon stagnation pressure of 1.5 atm. The mass spectrum indicates the formation of a major sequence of heterocluster ions with the formula $Ti^+(OCH_3)_m(DME)_n$ ($m = 1$–3) (labeled b_n, c_n, and d_n), in which the methoxy groups are thought to be covalently bonded to the titanium ions. The predominance of this sequence indicates that CH_3 elimination is the preferred decomposition pathway in the reactions of the Ti^+ ions within the parent $Ti^+(DME)_n$ (labeled a_n) cluster ions. The intact cluster ions $Ti^+(DME)_n$ stem from the association reaction between Ti^+ ions and dimethyl ether clusters, possibly followed by evaporation of some dimethyl ether molecules.

$$\begin{aligned} &Ti^+ + (DME)_m \rightarrow [Ti^+(DME)_m] \\ &\quad \rightarrow Ti^+(DME)_n + (m-n)DME \qquad (1) \end{aligned}$$

The evaporation of some dimethyl ether molecules is due to the excess kinetic energy of the laser-ablated Ti^+ ions and

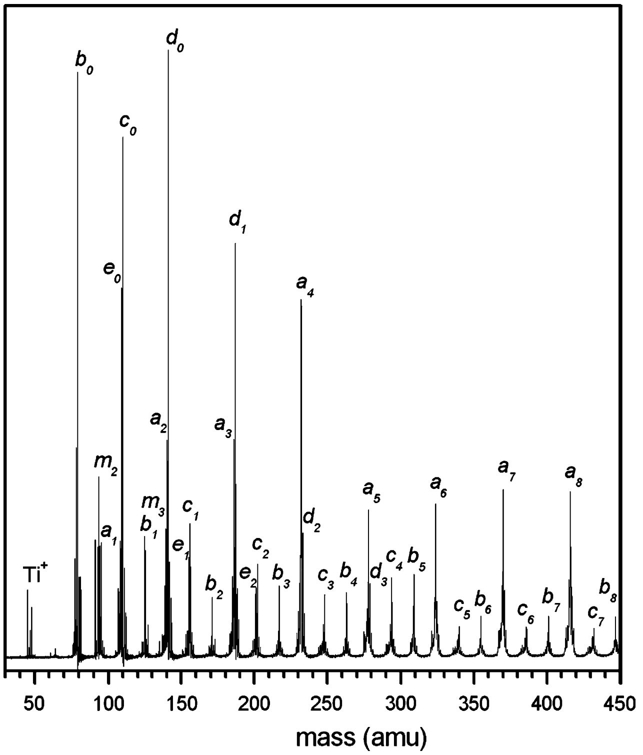


Fig. 1. Time-of-flight mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti^+ and dimethyl ether (CH_3OCH_3) clusters seeded in 1.5 atm. Ar. The laser fluence is 24 mJ/cm^2. a_n: $Ti^+(DME)_n$; b_n: $Ti^+(OCH_3)(DME)_n$; c_n: $Ti^+(OCH_3)_2(DME)_n$; d_n: $Ti^+(OCH_3)_3(DME)_n$; e_n: $Ti^+(OCH_2)(OCH_3)(DME)_n$; m_n: $(DME)_nH^+$. DME denotes CH_3OCH_3.

also the exothermicity of the ion–molecule association reaction. Considering the ionization energies (IEs) of these species, the positive charge should be located on the Ti atom because its IE (6.82 eV) is substantially lower than that of the dimethyl ether molecule (10.02 eV). Evidence supporting this claim has been provided by several beam experiments on the formation of metal ion-organic molecule or metal ion-rare gas clusters [22,23].

Univalent Ti^+ ions react with CH_3OCH_3 molecules, which contain one type of C–O bond and one type of C–H bond, via an oxidative addition mechanism. If Ti^+ inserts into the C–H bond of a DME molecule, a TiH^+ or $Ti^+CH_2OCH_3$ ion is expected to form from the $[H–Ti^+–CH_2OCH_3]$ intermediate after simple Ti^+–C or Ti^+–H bond breakage, respectively. However, these product ions are not observed in the mass spectrum, indicating that this C–H insertion reaction does not occur within the heteroclusters. Thermodynamic data indicate that the $H_3C–OCH_3$ bond dissociation energy is 83.3 kcal/mol [24], which is less than that of the $H–CH_2OCH_3$ bond (96.2 kcal/mol) [25]. Thus, the insertion of a Ti^+ ion into a C–O bond seems more energetically favorable than insertion into a C–H bond. Burnier et al. [2] have reported that Fe^+ reacts with dimethyl ether to produce $Fe(CH_2O)^+$ and CH_4 through a mechanism involving metal insertion into the polar C–O bond, followed by a β-hydride shift from the alkoxy ligand. Similarly, the ion–molecule reactions of Ti^+ with CH_3OCH_3 that arise from C–O bond insertion can be represented by the following reactions:

$$Ti^+ + CH_3OCH_3 \rightarrow Ti^+OCH_3 + CH_3 \qquad (2)$$

$$Ti^+ + CH_3OCH_3 \rightarrow Ti^+CH_3 + OCH_3 \qquad (3)$$

$$Ti^+ + CH_3OCH_3 \rightarrow TiO^+ + C_2H_6 \qquad (4)$$

$$Ti^+ + CH_3OCH_3 \rightarrow Ti^+OCH_2 + CH_4 \qquad (5)$$

The enthalpies of the observed reaction pathways were estimated from thermodynamic data [25–28] and are listed in Table 1.

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 [26]. 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 [29]. 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 CH_3OCH_3/Ar. In addition, the failure to observe any reaction products from the endothermic reaction channels even at high laser fluence supports our

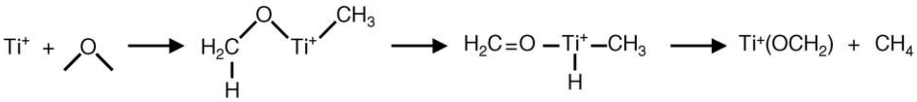
Table 1
Energetics for the possible reaction pathways of Ti^+ with ether molecules[a]

Reactant	Insertion site	Products	Enthalpy (kcal/mol)
CH_3OCH_3	C—O bond	$Ti^+OCH_3 + CH_3$	−28.2[b]
		Ti^+CH_3	25.4
		$TiO^+ + C_2H_6$	−75.2
		$Ti^+OCH_2 + CH_4$	−110.0[b]
$CH_3OCH_2CH_2CH_3$	C—O bond	$Ti^+OCH_3 + C_3H_7$	−26.0
		$Ti^+OC_3H_7 + CH_3$	−29.3[b]
	C—C bond	$Ti^+CH_3OCH_2 + C_2H_5$	28.3[c]
$CH_3OC(CH_3)_3$	C—O bond	$Ti^+OCH_3 + C(CH_3)_3$	−26.8
		$Ti^+OC(CH_3)_3 + CH_3$	−30.2[b]

[a] Reaction enthalpies were calculated from the thermochemical data provided in [25–28].

[b] The bond energy $D_0(Ti^+—OR)$ (R = CH_3, CH_2, C_3H_7, $C(CH_3)_3$) is assumed to equal $D_0(Ti^+—OH)$.

[c] The bond energy $D_0(Ti^+—CH_3OCH_2)$ is assumed to equal $D_0(Ti^+—CH_3)$.



Scheme 1.

hypothesis that Ti^+ ions in high-lying states make no appreciable contribution to the above reactions.

The complete absence of Ti^+CH_3 ion signals in the mass spectrum suggests that reaction (3) is energetically unfavorable; its enthalpy change is endothermic, 25.4 kcal/mol. The TiO^+ formation channel can proceed from the $[H_3C–Ti^+–OCH_3]$ intermediate through a four-centered transition state [12]. The TiO^+ ion can also be produced from the intermediate by β-methyl radical transfer to the metal ion, forming C_2H_6, which is then lost as a neutral product [30]. However, the fact that only negligible contributions from TiO^+ ions were observed in the mass spectrum demonstrates that the C_2H_6 elimination pathway (either via a four-centered transition state or CH_3 migration) is a less efficient route than the CH_3 elimination channel (reaction (2)) that produces $Ti^+(OCH_3)_m(CH_3OCH_3)_n$ ions, even though the former process is more exothermic than the latter.

We speculate that the methoxy-rich heterocluster ions are produced as a result of the consumption of $Ti^+(DME)_n$ ions by sequential intracluster ion–molecule reactions:

$$[Ti^+(DME)_n]^{\ddagger} \rightarrow Ti^+(OCH_3)(DME)_{n-1} + CH_3 \qquad (6)$$

$$[Ti^+(DME)_n]^{\ddagger} \rightarrow Ti^+(OCH_3)_2(DME)_{n-2} + 2CH_3 \qquad (7)$$

$$[Ti^+(DME)_n]^{\ddagger} \rightarrow Ti^+(OCH_3)_3(DME)_{n-3} + 3CH_3 \qquad (8)$$

The initial interaction between Ti^+ ions and DME molecules within the heteroclusters is envisioned to be with the more basic site on oxygen atom. The bonding in the association complex has been found to involve the formation of a dative bond requiring electron donation from the DME molecule to the 3d orbital of the Ti atom [31]. The Ti^+ ion then inserts into the C–O bond to form $[CH_3–Ti^+–OCH_3]$, after which Ti^+OCH_3 is formed via CH_3 elimination. This mechanism is in reasonable agreement with the results of Allison and Ridge [15], who reported that the ion–molecule reactions of chlorotitanium ions $TiCl_n{}^+$ (n = 1–3) with DME lead to methoxychlorotitanium ions, as shown in reaction (9).

$$TiCl_n^+ + CH_3OCH_3 \rightarrow TiCl_{n-1}OCH_3^+ + CH_3Cl \quad (n = 1, 2, 3) \qquad (9)$$

The further reactions of Ti^+OCH_3 ions with solvated CH_3OCH_3 molecules give rise to $Ti^+(OCH_3)_2$ and $Ti^+(OCH_3)_3$. A surprising implication of this series of cluster reactions is that CH_3 elimination from CH_3OCH_3 by the Ti^+ ion is only possible for up to three dimethyl ether molecules. The absence of cluster ions with the formula $Ti^+(OCH_3)_4(CH_3OCH_3)_n$ in the mass spectrum suggests that the coordination of three OCH_3 groups around a Ti^+ ion greatly reduces the ability of Ti^+ to break the C–O bonds of additional dimethyl ether molecules. We reached similar conclusions in our recent studies of the reactions of Ti^+ with alcohol clusters [19,20]. Because the Ti^+ ion has three valence electrons, this decrease in reactivity is primarily attributable to the large binding energy change that results from trivalent bond formation with three ligands with methoxy groups. This interpretation is consistent with the tetravalent structures commonly observed for neutral titanium compounds such as $TiCl_4$ and $Ti(OR)_4$, where R = CH_3, isopropyl, and *tert*-butyl.

Another observed reaction channel is the molecular elimination of CH_4 (reaction (5)). The mass spectrum indicates that $Ti^+(OCH_2)(OCH_3)(DME)_n$ ions (labeled e_n) are formed as reaction products but with much lower intensity. The observation of these ions indicates that $Ti^+(OCH_3)$ formed from the ion–molecule reaction $Ti^+ + CH_3OCH_3$ can undergo subsequent CH_4 elimination reactions with DME within the clusters. Reaction (5) is exothermic with an enthalpy change of 110 kcal/mol, suggesting that this reaction will occur when energetically feasible. Scheme 1 shows a proposed mechanism for the reaction of Ti^+ with DME. This mechanism is similar to that for the $Ti^+ + H_2O \rightarrow TiO^+ + H_2$ reaction, in which an $H_2Ti^+–O$ intermediate can form from an O–H bond insertion because Ti^+ has three valence electrons [30]. However, the fact that only minor contributions from TiO^+CH_2 ions are evident in the mass spectrum demonstrates that the CH_4 elimination channel via hydrogen migration is less efficient than the CH_3 elimination pathway (reaction (2)).

The intensities of the peaks corresponding to $Ti^+(DME)_n$ cluster ions in the mass spectrum in Fig. 1 are much lower than those corresponding to $Ti^+(OCH_3)_3(DME)_{n-2}$ cluster ions, for all clusters with $n \leq 3$. As the cluster size increases, however, the peaks corresponding to $Ti^+(DME)_n$ cluster ions become dominant. These results show that the reactivity of the Ti^+ ion diminishes with increasing solvation by dimethyl ether molecules. The same tendency has been found in the case of the reactions between Mg^+ and $(H_2O)_n$: the dominant products are $Mg^+(OH)(H_2O)_{n-1}$ for $n < 15$, whereas the intact cluster ions $Mg^+(H_2O)_n$ are the dominant species for $n \geq 15$ [32]. This apparent quenching of CH_3 elimination reactions is perhaps due to an increase in the stabilization of $Ti^+(DME)_n$ cluster ions as the degree of solvation increases. Another possibility is that the dimethyl ether molecules surrounding each metal ion create an energy barrier in the reaction pathway for CH_3 elimination. Because the ease of CH_3 radical transport within the tightly packed $Ti^+(DME)_n$ cluster ion solvent cage after C–O bond cleavage is greatly reduced, the probability that a CH_3 radical eliminated from CH_3OCH_3 will become trapped is expected to increase with cluster size [33]. This increase in trapping probability would be expected

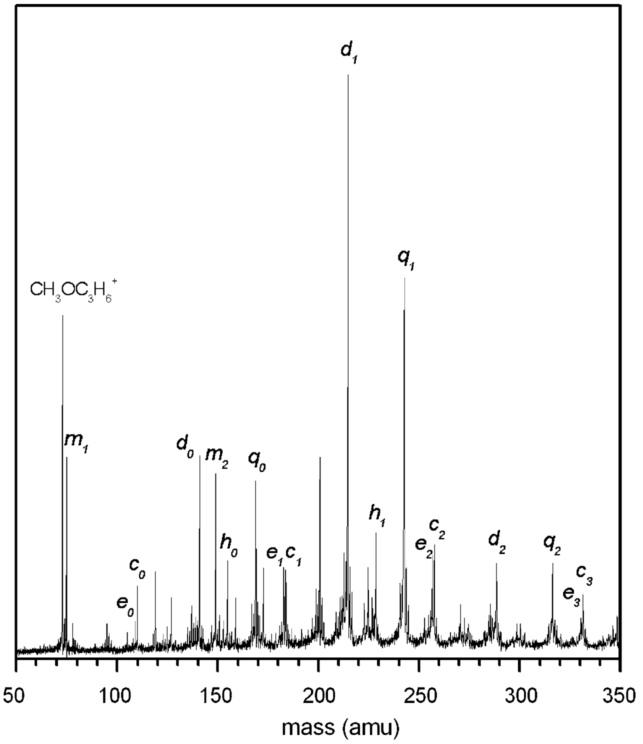


Fig. 2. Time-of-flight mass spectrum showing the ions produced by the reactions of Ti^+ with methyl propyl ether ($CH_3OCH_2CH_2CH_3$) clusters. c_n: $Ti^+(OCH_3)_2(MPE)_n$; d_n: $Ti^+(OCH_3)_3(MPE)_n$; e_n: $Ti^+(OCH_2)(OCH_3)(MPE)_n$; h_n: $Ti^+(OCH_3)_2(CH_3OCH_2)(MPE)_n$; q_n: $Ti^+(OCH_3)_2(OC_3H_7)(MPE)_n$; m_n: $(MPE)_nH^+$. MPE denotes $CH_3OCH_2CH_2CH_3$.

to suppress CH_3 elimination reactions in sufficiently large clusters.

3.2. The reactions of Ti^+ ions with methyl n-propyl ether clusters

The presence of the $CH_3CH_2CH_2$ group in methyl *n*-propyl ether is expected to result in cluster reaction pathways that are different to those of dimethyl ether, because $CH_3OCH_2CH_2CH_3$ (MPE) contains C–O, C–C, and C–H bonds. Thus, studying the $Ti^+ + CH_3OCH_2CH_2CH_3$ system offers an opportunity to investigate the chemical reactivity of Ti^+ with respect to its insertion reactions with three different chemical bonds. The mass spectrum obtained using a laser pulse energy of 28 mJ/cm^2 and an argon stagnation pressure of 1.5 atm is presented in Fig. 2. The dominant cluster ions belong to the series of heterocluster ions, $Ti^+(OCH_3)_m(MPE)_n$ ($m = 2$, 3) (labeled c_n and d_n) and $Ti^+(OCH_3)_2(OC_3H_7)(MPE)_n$ (labeled q_n), which result from sequential alkyl radical eliminations. These alkyl radical elimination reactions occur for up to three MPE molecules, which is similar to the behavior observed for the $Ti^+ + CH_3OCH_3$ system. The absence of $Ti^+(OC_3H_7)_m(MPE)_n$ ions strongly suggests that the Ti^+ ion inserts selectively into the C–O bond of the *n*-propoxy group to form the intermediate $[CH_3O–Ti^+–C_3H_7]$, leading to Ti^+OCH_3 formation after *n*-C_3H_7 elimination. The reaction enthalpies of $Ti^+ + MPE \rightarrow Ti^+OCH_3 + C_3H_7$ ($\Delta H = -26.0$ kcal/mol) and $Ti^+ + MPE \rightarrow Ti^+OC_3H_7 + CH_3$ ($\Delta H = -29.3$ kcal/mol) are similar, so the selectivity of this insertion is presumably due to the electron-rich character of the *n*-propyl group. The predominant formation of Ti^+OCH_3 from the $[CH_3O–Ti^+–C_3H_7]$ intermediate is also plausible, because the energy required for the bond dissociation D_0° of $Ti^+–C_3H_7$ (57 kcal/mol) [26] is much lower than that of $Ti^+–OCH_3$ (111 kcal/mol), assuming that $D_0^\circ(Ti^+–OCH_3)$ is equal to $D_0^\circ(Ti^+–OH)$ [28].

The formation of $Ti^+(OCH_2)(OCH_3)(MPE)_n$ (e_n series) indicates that Ti^+ reacts with methyl *n*-propyl ether to produce $Ti^+(OCH_2)$ and C_3H_8 through a mechanism involving metal insertion into the polar C–O bond followed by an acidic hydrogen shift from the methoxy ligand. The reaction products $Ti^+(OCH_3)_2(CH_3OCH_2)(MPE)_n$ (labeled h_n) are also observed, but at much lower intensities. This implies that each $Ti^+(OCH_3)_2$ ion reacts further in sequential C–C bond insertions followed by C_2H_5 elimination to form $Ti^+(OCH_3)_2(CH_3OCH_2)$. This result demonstrates that C–O bond insertion competes more strongly with C–C bond insertion as the chain length of the alkyl radical increases.

3.3. The reactions of Ti^+ ions with methyl n-butyl ether clusters

Fig. 3 shows a typical TOF mass spectrum of the products of reaction between Ti^+ and methyl *n*-butyl ether (MNBE, $CH_3OCH_2CH_2CH_2CH_3$) clusters. Methyl *n*-butyl ether possesses a longer alkyl chain than dimethyl ether and methyl *n*-propyl ether, so there is a higher probability of Ti^+ insertion reactions within the heteroclusters. Some of the prominent peaks in this spectrum correspond to the heterocluster ions $Ti^+(OCH_3)_2(MNBE)_n$ (labeled c_n), which can arise from Ti^+ insertion into the C–O bond of an *n*-butoxy group to form the intermediate $[CH_3O–Ti^+–C_4H_9]$ followed by C_4H_9 elimination. The observation of minor contributions from $Ti^+(OCH_3)(OC_4H_9)(MNBE)_n$ and $Ti^+(OCH_3)_2(OC_4H_9)(MNBE)_n$, labeled p_n and q_n, respectively, also supports our previous conclusion that Ti^+ ion insertion occurs preferentially into the C–O bond of the *n*-butoxy group rather than into the methoxy group, as was observed for the $Ti^+ + CH_3OCH_2CH_2CH_3$ system.

Another series of dominant peaks in the mass spectrum correspond to $Ti^+(CH_3OCHCH_2)(MNBE)_n$ (labeled o_n), formed from alkane (C_2H_6) elimination reactions in intact cluster ions $Ti^+(MNBE)_n$. Blomberg and coworkers have reported that C_2H_6/C_2D_6 eliminations resulting from the reactions of Ni^+ ions within *n*-C_4H_{10}/*n*-C_4D_{10} heterocluster ions follow the initial insertion of Ni^+ into the central C–C bond, the weakest bond in the alkane [34]. As shown in Scheme 2, the formation of the $Ti^+(CH_3OCHCH_2)$ ion is ascribed to the insertion of a Ti^+ ion into the cen-

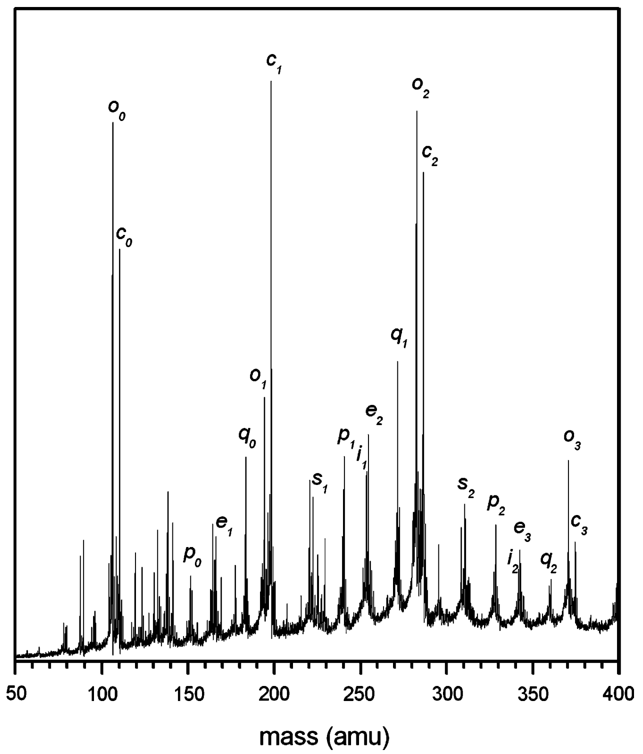


Fig. 3. Time-of-flight mass spectrum showing the ions produced by the reactions of Ti^+ with methyl *n*-butyl ether ($CH_3OCH_2CH_2CH_2CH_3$) clusters. a_n: $Ti^+(MNBE)_n$; c_n: $Ti^+(OCH_3)_2(MNBE)_n$; i_n: $Ti^+(OCH_3)(CH_3OC_4H_7)(MNBE)_n$; o_n: $Ti^+(CH_3OCHCH_2)(MNBE)_n$; p_n: $Ti^+(OCH_3)(OC_4H_9)(MNBE)_n$; q_n: $Ti^+(OCH_3)_2(OC_4H_9)(MNBE)_n$; s_n: $Ti^+(CH_3OC_4H_7)(MNBE)_n$; e_n: $Ti^+(OCH_2)(MNBE)_n$. MNBE denotes $CH_3OCH_2CH_2CH_2CH_3$.

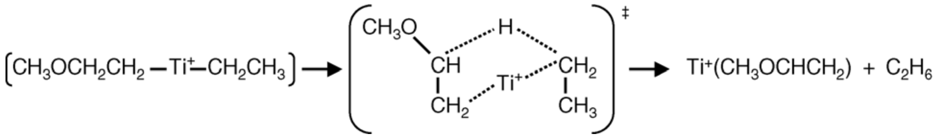
tral C–C bond (the weakest bond in the alkyl radical) of an *n*-butyl group and subsequent β-hydrogen migration to form $Ti^+(CH_3OCHCH_2)(C_2H_6)$, from which C_2H_6 elimination occurs.

It is noted that the reactions of Ti^+ with MNBE clusters give rise to the H_2 elimination products by C–H bond insertion pathways; these products include $Ti^+(OCH_3)(CH_3OC_4H_7)(MNBE)_n$ and $Ti^+(CH_3OC_4H_7)$-$(MNBE)_n$ ions (labeled i_n and s_n, respectively). Recently, Jerzy and coworkers have reported the reactions of Ti^+ with ethane, $Ti^+ + C_2H_6 \rightarrow Ti^+C_2H_4 + H_2$, for which H_2 elimination products are observed [35]. For the reactions of Co^+, Ni^+, and Fe^+ ions with hydrocarbons such as C_2H_6, C_3H_8, and C_4H_{10}, H_2 elimination products have also been observed [36–40]. Tolbert and Beauchamp have also investigated the reactions of Ti^+ with several deuterium-labeled alkanes by using an ion beam apparatus [10]. The alkanes were found to be cleaved by the metal ion through oxidative-addition reactions, which were explained as arising from C–H insertions leading to 1,2-hydrogen eliminations. The observation of dehydrogenation products in the reactions of Ti^+ with MNBE indicates the possibility of insertion of Ti^+ into the C–H bond on the extended alkyl chain of an ether molecule.

3.4. *The reactions of Ti^+ ions with methyl t-butyl ether clusters*

The *t*-butyl group is a particularly interesting substituent because of its high intrinsic stability and bulkiness. A typical TOF mass spectrum of the products of reaction between Ti^+ and methyl *t*-butyl ether (MTBE, $CH_3OC(CH_3)_3$) clusters is displayed in Fig. 4. The spectrum in the low mass region indicates the formation of a sequence of $(MTBE)_nH^+$ (labeled m_n) cluster ions, which can be attributed to the protonation of the generated parent cluster ion. Similar results have also been reported in the electron and chemical ionization mass spectrum of MTBE using a Fourier transform ion cyclotron resonance (FTICR) cell [41]. These species presumably derive from electron impact ionization by free electrons escaping from the expanding plasma of laser ablation. In a recent study of the photoionization of MTBE that used supersonic expansion and time-of-flight mass spectrometry, Chambreau and coworkers reported that MTBE does not produce an intense molecular ion peak, but loses a methyl radical to form an *O*-methylated acetone ion, $(CH_3)_2C=OCH_3{}^+$ (*m/z* 73) [42]. $(CH_3)_2C=OCH_3{}^+(MTBE)_n$ (labeled n_n) cluster ions might be produced by the charge transfer reaction $Ti^+ + (MTBE)_n \rightarrow Ti + (MTBE)_n^+$ due to the relatively low ionization energy of MTBE (9.24 eV) compared with those of DME (10.02 eV), MPE (9.41 eV), and MNBE (9.40 eV). The ionized MTBE molecules undergo subsequent α-cleavage fragmentation within the clusters, which is a characteristic reaction of tertiary ethers.

The observation of dominant mass peaks corresponding to $Ti^+(OCH_3)_m(MTBE)_n$ ($m = 2, 3$) (labeled c_n and d_n) ions is quite surprising since the reaction $Ti^+ + MTBE \rightarrow Ti^+O$-$C(CH_3)_3 + CH_3$ ($\Delta H = -30.2$ kcal/mol) is more exothermic than the $Ti^+ + MTBE \rightarrow Ti^+OCH_3 + C(CH_3)_3$ channel ($\Delta H = -26.8$ kcal/mol). Moreover, it is unlikely that the insertion of a Ti^+ ion into the C–O bond of a *t*-butoxy group occurs to form a $[CH_3O\text{–}Ti^+\text{–}C(CH_3)_3]$ intermediate because of the steric hindrance by the *t*-butyl radical. The preference in this system for $O\text{–}C(CH_3)_3$ bond insertion is probably because the electron donating *t*-butyl group attracts the Ti^+ ion more effectively. In addition, the elimination of a *t*-butyl radical after the formation of a $[CH_3O\text{–}Ti^+\text{–}C(CH_3)_3]$ inter-



Scheme 2.

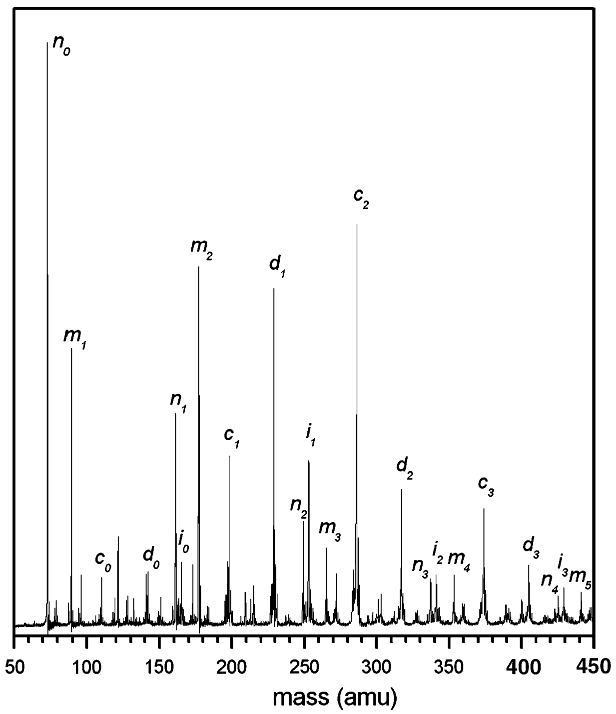


Fig. 4. Time-of-flight mass spectrum showing the ions produced by the reactions of Ti^+ with methyl *t*-butyl ether $CH_3OC(CH_3)_3$ clusters. c_n: $Ti^+(OCH_3)_2(MTBE)_n$; d_n: $Ti^+(OCH_3)_3(MTBE)_n$; i_n: $Ti^+(OCH_3)(CH_3OC_4H_7)(MTBE)_n$; m_n: $(MTBE)_nH^+$; n_n: $(CH_3)_2C{=}OCH_3{}^+(MTBE)_n$. MTBE denotes $CH_3OC(CH_3)_3$.

mediate is energetically more favorable than the elimination of CH_3, *n*-C_3H_7, or *n*-C_4H_9 radicals, as shown in the present study. The total absence of $Ti^+(OCH_3)_x(OC_4H_9)_y(MTBE)_n$ ions supports our conclusion that Ti^+ insertion into the C–O bond of a *t*-butoxy group in a MTBE molecule followed by *t*-butyl radical elimination is the predominant pathway.

Further, the observation of mass peaks corresponding to $Ti^+(OCH_3)(CH_3OC_4H_7)(MTBE)_n$ (labeled i_n) ions is primarily attributable to the elimination of a H_2 molecule after Ti^+ insertion into the C–H bond of a *t*-butyl radical. The preference of this system for H_2 elimination from the *t*-butyl radical is explained by proposing that the reaction path degeneracy of the nine equivalent C–H insertion sites on the *t*-butyl group dominates over the three equivalent C–H insertion sites on the methyl group. The hypothesis of a H_2 elimination reaction from the *t*-butyl group is also supported by the fact that H_2 elimination products are not observed in the $Ti^+ + CH_3OCH_3$ system. However, the lower intensity in the mass spectrum of the i_n series than those of $C(CH_3)_3$ elimination products such as $Ti^+(OCH_3)_m(MTBE)_n$ clusters implies that C–H activation is energetically less favorable than activation of the C–O bond of the *t*-butoxy group. The thermodynamic data show that the C–H bond dissociation energy (98.0 kcal/mol) [43] of the *t*-butyl group is larger than that of the C–O bond (84.3 kcal/mol).

4. Conclusion

The reactions that proceed within mixed titanium-ether cluster ions were studied using the laser ablation-molecular beam method. The primary reactions of Ti^+ ions with CH_3OR ($R = CH_3$, *n*-C_3H_7, *n*-C_4H_9, *t*-C_4H_9) clusters appear to be the cleavage of the three bonds in these molecules: i.e., C–O, C–C, and C–H insertions, with C–O bond insertion the dominant process. A major sequence of methoxy-rich fragment ions $Ti^+(OCH_3)_m(CH_3OR)_n$ ($m = 1$–3) is attributed to the selective insertion of Ti^+ ions into the C–O bonds of OR groups in the ether molecules, followed by R elimination. In addition, it was found that each Ti^+ ion can produce alkyl radical elimination in up to three ether molecules, as a result of consecutive insertion reactions of Ti^+ ions within the heteroclusters, leading to the formation of $Ti^+(OCH_3)_x(OR)_y(CH_3OR)_n$ ($x + y = 3$) ions. The experiments also show that the chemical reactivity of Ti^+-ether heterocluster ions is greatly influenced by cluster size and by the nature of the alkyl group of the ether molecules. By examining the products of the reactions of Ti^+ with dimethyl ether, methyl *n*-propyl ether, and methyl *n*-butyl ether, we conclude that the reaction products resulting from C–C and C–H bond insertions become more important as the size of the alkyl groups (R) in the ether molecules increases.

Acknowledgements

This work was supported by the Korea Research Foundation Grant (KRF-2000-015-DP0203). One of the authors (K.-W.J.) also gratefully acknowledges Wonkwang University for the partial support of this research in 2002.

References

[1] J. Allison, D.P. Ridge, J. Am. Chem. Soc. 101 (1979) 4998.
[2] R.C. Burnier, G.D. Byrd, B.S. Freiser, J. Am. Chem. Soc. 103 (1981) 4360.
[3] P.B. Armentrout, J.L. Beauchamp, J. Chem. Phys. 74 (1981) 2819.
[4] P.B. Armentrout, J.L. Beauchamp, J. Am. Chem. Soc. 103 (1981) 784.
[5] P.B. Armentrout, L.F. Halle, J.L. Beauchemp, J. Am. Chem. Soc. 103 (1981) 6501.
[6] P.B. Armentrout, J.L. Beauchamp, Chem. Phys. 50 (1980) 37.
[7] L.F. Haale, P.B. Armentrout, J.L. Beauchamp, Organometallics 1 (1982) 963.
[8] P.B. Armentrout, L.F. Halle, J.L. Beauchamp, J. Am. Chem. Soc. 103 (1981) 6624.
[9] G.D. Byrd, R.C. Burnier, B.S. Freiser, J. Am. Chem. Soc. 104 (1982) 3565.
[10] M.A. Tolbert, J.L. Beauchamp, J. Am. Chem. Soc. 108 (1986) 7509.
[11] S.S. Yi, R.J. Noll, J.C. Weisshaar, J. Phys. Chem. A 103 (1999) 7254.
[12] E.L. Reicher, J.C. Weisshaar, J. Phys. Chem. A 106 (2002) 5563.
[13] S.S. Yi, M.R.A. Blomberg, P.E.M. Siegbahn, J.C. Weisshaar, J. Phys. Chem. A 102 (1998) 395.

[14] D.E. Clemmer, Y.-M. Chen, N. Aristov, P.B. Armentrout, J. Phys. Chem. 98 (1994) 7538.

[15] J. Allison, D.P. Ridge, J. Am. Chem. Soc. 100 (1978) 163.

[16] D.N. Shin, K.-W. Jung, K.-H. Jung, J. Am. Chem. Soc. 114 (1992) 6926.

[17] S.-S. Choi, K.-W. Jung, K.-H. Jung, Int. J. Mass Spectrom. Ion Process. 124 (1993) 11.

[18] S.Y. Lee, D.N. Shin, S.G. Cho, K.-H. Jung, K.-W. Jung, J. Mass Spectrom. 30 (1995) 969.

[19] Y.M. Koo, J.H. Kim, H. Lee, K.-W. Jung, J. Phys. Chem. A 106 (2002) 2465.

[20] Y.M. Koo, H.J. An, S.-K. Yoo, K.-W. Jung, Int. J. Mass Spectrom. 226 (2003) 305.

[21] Y.M. Koo, H.J. An, S.-K. Yoo, K.-W. Jung, Bull. Korean Chem. Soc. 24 (2003) 197.

[22] J.S. Pilgrim, C.S. Yeh, K.R. Berry, M.A. Duncan, J. Chem. Phys. 100 (1994) 7945.

[23] P. Weis, P.R. Kemper, M.T. Bowers, J. Phys. Chem. A 101 (1997) 8207.

[24] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.

[25] D.R. Lide, CRC Handbook of Chemistry and Physics, 81th ed., CRC Press, London, 2000.

[26] L.S. Sunderlin, P.B. Armentrout, J. Phys. Chem. 92 (1988) 1209.

[27] M.W. Chase, J.L. Curnutt, H. Prophet, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data 4 (1975) 1.

[28] D.E. Clemmer, N. Aristiv, P.B. Armentrout, J. Phys. Chem. 97 (1993) 544.

[29] Y.-M. Chen, D.E. Clemmer, P.B. Armentrout, J. Phys. Chem. 98 (1994) 11490.

[30] S.W. Buckner, J.R. Gord, B.S. Freiser, J. Am. Chem. Soc. 110 (1988) 6606.

[31] D.B. Pedersen, M.Z. Zgierski, S. Anderson, D.M. Rayner, B. Simard, S. Li, D.-S. Yang, J. Phys. Chem. A 105 (2001) 11462.

[32] F. Misaizu, M. Sanekata, K. Fuke, S. Iwata, J. Chem. Phys. 100 (1994) 1161.

[33] W. Lu, S. Yang, J. Phys. Chem. A 102 (1998) 825.

[34] M. Blomberg, S.S. Yi, R.J. Noll, J.C. Weisshaar, J. Phys. Chem. A 103 (1999) 7254.

[35] M. Jerzy, D.G. Fedorov, M.S. Gordon, J. Chem. Phys. 112 (2000) 10247.

[36] E.L. Reichert, J.C. Weisshaar, J. Phys. Chem. A 106 (2002) 5563.

[37] D.G. Fedorov, M.S. Gordon, J. Phys. Chem. A 104 (2000) 2253.

[38] S.S. Yi, M.R.A. Blomberg, P.E.M. Siegbahn, J.C. Weisshaar, J. Phys. Chem. A 102 (1998) 395.

[39] R. Tonkyn, M. Ronan, J.C. Weisshaar, J. Phys. Chem. 92 (1988) 92.

[40] R. Tonkyn, J.C. Weisshaar, J. Phys. Chem. 90 (1986) 2305.

[41] M. Buchner, H.F. Grutzmacher, Int. J. Mass Spectrom. 199 (2000) 141.

[42] S.D. Chambreau, J. Zhang, J.C. Traeger, T.H. Morton, Int. J. Mass Spectrom. 199 (2000) 17.

[43] Ch. George, H. El Rassy, J.-M. Chovelon, Int. J. Chem. Kinet. 33 (2001) 539.