on the determination of IP(SF_5) ≤ IP(NH_3) = 10.14 eV[14,32] but which has been shown subsequently to be too large. The corrected value IP(SF_5) = 9.65 ± 0.05 eV[31] leads to AP(SF_5^+/SF_6) = 13.60 eV and $\Delta H_f(SF_5^+)$ = 12 kJ mol^{-1}. This reduced value of ΔH_f(SF_5^+) was anticipated recently by the observation of the reaction

$$HBr^+ + SF_6 \rightarrow SF_5^+ + HF + Br$$

which has been reported by Tichy et al.[33] to proceed at the collision rate requiring AP(SF^+/SF_6) < 13.87 ± 0.04 eV. In consequence, reaction 1 reported here is more exothermic than indicated by the ΔH values detailed in Table I and within the text: i.e., ΔH_1 = −49 kJ mol^{-1}.

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Formation and Fragmentation of Gas-Phase Titanium/Oxygen Cluster Positive Ions

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Abstract: Positive ions of titanium/oxygen clusters have been investigated with mass spectrometry and collision-induced dissociation. The cluster ions were produced by sputtering titanium dioxide powder and titanium foil (exposed to oxygen) with an energetic (8 keV) xenon atom beam. Titanium/oxygen cluster ions sputtered from the foil were seen to have the form $[Ti_nO_{2n-\delta}]^+$, where n equals 1 to 8 and δ ranges from 0 to 4. Sputtering titanium dioxide powder yields abundant $[Ti_nO_{2n-\delta}]^+$ clusters, where n equals 1 to 7 and δ = 1, 2, and 3. Titanium foil sputtered in a high-pressure (0.1–0.2 Torr) fast-atom bombardment (HPFAB) ion source with O_2 produces $[Ti_nO_{2n-1}]^+$ cluster ions as the only abundant cluster species. The collision-induced dissociation spectra of $[Ti_nO_{2n-\delta}]^+$ clusters show mainly losses of Ti, TiO, and TiO_2 moieties. Mass-selected $[Ti_nO_{2n-\delta}]^+$ cluster ions also react hyperthermically with O_2 in the collision quadrupole of a tandem mass spectrometer to form $[Ti_nO_{2n-1}]^+$ clusters. A simple pair-potential ionic model was used to calculate energy-optimized geometric structures of the clusters. Distinct structural differences between the Ti_nO_{2n-2} and Ti_nO_{2n-1} clusters were not found, whereas the lowest energy Ti_nO_{2n} isomers were found to have pendant and terminal oxygen atoms. For both titanium/oxygen and cobalt/oxygen clusters, the pair-potential model identifies the most abundant clusters as those having the lowest calculated energy per atom.

Introduction

There is tremendous interest in characterizing the chemistry of gas-phase metal/oxygen ions[1-5] and clusters.[6-8] An early study of gas-phase metal cluster reactions reported the reactivity of Mn_2^+ with O_2 to form Mn^+, MnO^+, and Mn_2O^+.[9] Anderson and co-workers[10-12] as well as Jarrold and Bower[13-15] have studied the reactions of Al_n^+ clusters with O_2. The reactions of Cu_n^+ clusters with O_2 have been studied with FTMS.[16] The reactions of homo- and heterogeneous di- and trimethyl cobalt and iron ions with O_2 have been studied with FTMS.[17] In this latter study, the cluster ions were formed by electron ionization of the corresponding volatile metal carbonyl followed by multistep reaction sequences to form the desired precursor(s). Thermochemical data from these studies suggest the formation of bridged oxide species for $[M'MO]^+$, $[M'MO_2]^+$, and $[M'M_2O_3]^+$ (M, M′ = Fe, Co). Thus, the role of structure in determining the reactivity of metal/oxygen cluster ions needs to be addressed. To answer that question, the types and structures of metal/oxygen cluster ions that can be produced must be determined.

We have previously reported studies of the formation, fragmentation, and reactions of cobalt/oxygen cluster ions.[18,19] The cluster ions were formed by sputtering Co in the presence of O_2 (0.1 Torr). Two major classes of cluster ions were observed: $[Co_nO_{n-1}]^+$ and $[Co_nO_n]^+$. Collision-induced dissociation (CID) was used to obtain structural information for the cobalt/oxygen cluster ions.[18] In general, the fragment ions produced had the stoichiometry $[Co_xO_x]^+$. This corresponds to losses of Co_yO_y (y = 1–3) from the $[Co_nO_n]^+$ clusters and to losses of Co_yO_{y-1} (y = 1–3) from the $[Co_nO_{n-1}]^+$ clusters. Geometric structures of the cobalt/oxygen cluster ions were calculated with use of a simple Coulomb plus Born-Mayer pair-potential model. The Co_nO_{n-1}

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Table I. Collision-Induced Dissociations of $[Ti_nO_{2n-\delta}]^+$ Cluster Ions

precursor			fragment ion		neutral fragment		relative abundance[a]		
n	δ	stoichiometry	δ	stoichiometry	δ	stoichiometry[b]	Ti[c]	TiO_2[d]	Ti + O_2[e]
4	1	$[Ti_4O_7]^+$	1	$[Ti_3O_5]^+$	0	TiO_2	100	100	100
			1	$[TiO]^+$	0	Ti_3O_6	50	25	50
	2	$[Ti_4O_6]^+$	1	$[Ti_3O_5]^+$	1	TiO	40	55	
			2	$[Ti_3O_4]^+$	0	TiO_2	100	100	
			1	$[TiO]^+$	1	Ti_3O_5		33	
	3	$[Ti_4O_5]^+$	2	$[Ti_3O_4]^+$	1	TiO	100		
	4	$[Ti_4O_4]^+$	2	$[Ti_3O_4]^+$	2	Ti	100		
3	1	$[Ti_3O_5]^+$	1	$[Ti_2O_3]^+$	0	TiO_2	40	25	40
			1	$[TiO]^+$	0	Ti_2O_4	100	100	100
	2	$[Ti_3O_4]^+$	4	$[Ti_3O_2]^+$		2O			90
			1	$[Ti_2O_3]^+$	1	TiO	100	100	100
			2	$[Ti_2O_2]^+$	0	TiO_2	12	5	
			1	$[TiO]^+$	1	Ti_2O_3	7		
	3	$[Ti_3O_3]^+$	2	$[Ti_2O_2]^+$	1	TiO	100		
	4	$[Ti_3O_2]^+$	2	$[Ti_2O_2]^+$	2	Ti	100		
			3	$[Ti_2O]^+$	1	TiO	12		
2	0	$[Ti_2O_4]^+$	1	$[Ti_2O_3]^+$		O	30	10	100
			3	$[Ti_2O]^+$		3O	100		
			0	$[TiO_2]^+$	0	TiO_2	10	100	40
			1	$[TiO]^+$	0	TiO_2, O		20	
	1	$[Ti_2O_3]^+$	1	$[TiO]^+$	0	TiO_2	100	100	100
	2	$[Ti_2O_2]^+$	4	$[Ti_2]^+$		2O			20
			0	$[TiO_2]^+$	2	Ti		36	
			1	$[TiO]^+$	1	TiO	100	100	100
	3	$[Ti_2O]^+$	1	$[TiO]^+$	2	Ti	15		
			2	Ti^+	1	TiO	100		

[a] Relative to 100 for the most abundant fragment ion. No correlation has been made for any possible metastable dissociations. No entry indicates that the channel was not observed and must be less than 0.1% of the base peak. [b] Neutral identities are inferred and may not correspond to intact fragments. [c] Results for cluster ions formed by sputtering Ti foil in a conventional FAB ion source and using Ar as a collision gas. [d] Results for cluster ions formed by sputtering TiO_2 in a conventional FAB ion source and using Ar as a collision gas. Under these conditions, the $[Ti_2O]^+$, $[Ti_3O_2]^+$, $[Ti_3O_3]^+$, $[Ti_4O_4]^+$, and $[Ti_4O_5]^+$ cluster ions were not abundant enough to obtain their collision spectra. [e] Results for cluster ions formed in the HPFAB ion source and using Ar as a collision gas. Under these conditions, the $[Ti_2O]^+$, $[Ti_3O_2]^+$, $[Ti_3O_3]^+$, $[Ti_4O_4]^+$, $[Ti_4O_5]^+$, and $[Ti_4O_6]^+$ cluster ions were not abundant enough to obtain their collision spectra.

Table II. Some Neutral Fragment Losses from Collision-Induced Dissociation of $[Ti_nO_{2n-\delta}]^+$ (δ = 0–4) Clusters[a]

neutral fragment	relative abundance[b]												
	$n = 2$					$n = 3$				$n = 4$			
	$\delta = 0$	$\delta = 1$	$\delta = 2$	$\delta = 3$	$\delta = 4$	$\delta = 1$[d]	$\delta = 2$	$\delta = 3$	$\delta = 4$	$\delta = 1$[e]	$\delta = 2$	$\delta = 3$	$\delta = 4$
Ti				15	100				100				100
TiO			100	100			100	100	12		40	100	
TiO_2	10	100				40	12			50	100		

[a] Results for cluster ions formed by sputtering Ti foil in a conventional FAB ion source. [b] Abundances are given relative to 100 for the most abundant product; that is, the neutral fragment loss that corresponds to the most abundant dissociation fragment ion. No correction has been made for any metastable dissociations. [c] Neutral fragment stoichiometries are inferred from fragment ion stoichiometries and may not correspond to intact fragments. [d] The loss of Ti_2O_4 was the most abundant process observed. [e] The fragment ion corresponding to the loss of Ti_3O_6 was observed to have a relative abundance of 50.

clusters were calculated to be strained and angular with protruding cobalt atoms. The Co_nO_n clusters were found to be symmetrical cubes, cages, rings, or ladders. In addition, classical dynamic trajectory calculations using the geometric structures yielded the same fragmentations that were observed in experiments. Reactions of the two classes of cluster ions were found to be dramatically different, and the differences were postulated to be due to structural differences in the compounds.[19]

We have undertaken further experiments to determine the chemistry of other first-row transition-metal oxygen cluster ions.[20] We present here our results on the formation and fragmentation of titanium/oxygen cluster positive ions using high-pressure fast-atom bombardment ionization[21,22] combined with tandem mass spectrometry.[23,24] We include in our discussion a comparison of calculated structures found for the titanium/oxygen clusters using a simple pair-potential model. In particular, the pair-po-

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tential model identifies for both titanium/oxygen and cobalt/oxygen clusters the most abundant clusters as those having the lowest calculated energy per atom.

Experimental Section

Titanium/oxygen cluster ions were produced by bombarding titanium foil or titanium dioxide powder with an energetic (8 keV) beam of xenon atoms. The sputtering occurred within a conventional fast-atom bombardment (FAB) ion source. After formation, the metal/oxygen cluster ions were accelerated to 8 keV and mass analyzed in a conventional manner with use of a hybrid, tandem mass spectrometer (EBQQ geometry),[25] which was also used to obtain low-energy collision spectra (discussed below). The identities of the clusters in the mass spectra were made by using a comparison of the expected isotopic abundances of Ti and by corroboration with the (relatively simple) fragmentations (Tables I and II, discussed below).

Titanium/oxygen cluster ions were also formed by sputtering metal foils in a high-pressure (0.1–1.0 mBar) fast-atom bombardment (HPFAB) ion source. The technique has proven useful in the study of metal cluster ion-molecule reactions.[18,19,26] Sputtered metal and metal/oxygen cluster ions and neutrals react with O_2 serving as a buffer/reactant gas to produce the observed metal/oxygen cluster ions. The reactant gas was admitted to the ion source at a pressure of 0.1–0.2 mBar. The pressure was measured by using a thermal conductivity gauge inserted into the ion source before and after performing the experiments. It was not possible to monitor the pressure during the experiments because of the high voltage present on the ion source (8 kV). An ionizing filament was not used in these experiments; the only mode of ionization was from interaction of the fast-atom beam, either by surface sputtering or by collisional ionization of neutral species.

The HPFAB source provides a unique ability to study cluster ion-molecule reactions at relatively high pressures (>0.1 mBar). At these pressures, the cluster ions can undergo tens to hundreds of collisions before exiting the ion source. This permits processes such as collisional stabilization of internally excited species.[22] The oxidation of a metal surface (or cluster) is exothermic[27] and thermalization or partial thermalization of translationally and internally hot ions can be accomplished via collisions with a buffer gas.[1,22,28]

Collision-induced dissociation (CID) experiments were performed with use of a hybrid (EBQQ configuration) tandem mass spectrometer. The collision-induced dissociation spectra were acquired by (i) mass selecting the precursor ions with use of the first mass spectrometer (EB), (ii) injecting the ions with 30–40 eV kinetic energy (lab coordinates) into the first quadrupole (collision cell Q_1) where they undergo collision-induced dissociation, and (iii) mass analyzing the fragment ions produced by using the second quadrupole (Q_2). Argon was used as the collision gas. The pressure in the collision cell was adjusted to reduce the precursor cluster ion intensity to about 50% of the original intensity. The collision energy of the ions was adjusted to optimize the fragmentation. That is, a collision energy was chosen above the threshold energy for all fragmentations to permit observation of all fragmentation channels. The abundances of fragmentations from measurements of CID spectra acquired at various times retained qualitative agreement. Relative and absolute abundances varied (±20%) because of the difficulty in exactly duplicating experimental conditions, including pressures of the reactant and collision gases and primary ion abundances. The stoichiometric identification of the CID fragments (^{48}Ti versus 3-^{16}O) may be ambiguous due to acquisition at unit mass resolution. However, the similarity of the fragmentation patterns between different cluster ion homologues suggests that our stoichiometric assignments are correct.

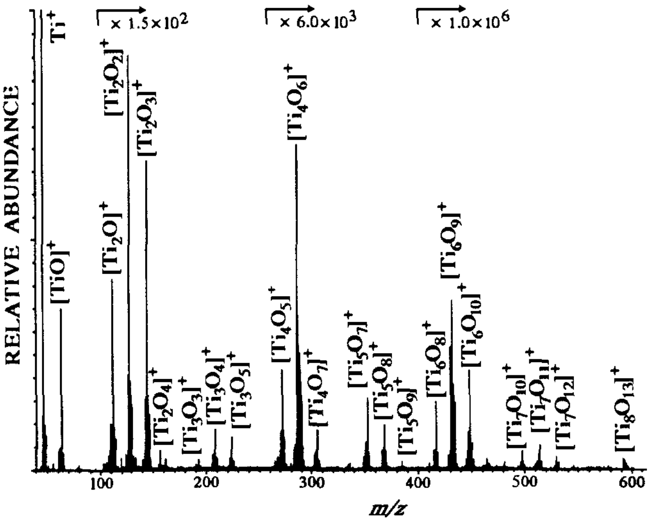

Figure 1. The FAB mass spectrum obtained from "pure" titanium foil. The predominant cluster ions have the stoichiometry $[Ti_nO_{2n-\delta}]^+$ where $n = 1$ to 8 and δ ranges from 1 to 4.

Hyperthermic reactions of the metal cluster ions were also studied in the first quadrupole collision cell. The experiment was performed as described above, with the exception of using O_2 as the collision/reactant gas in Q_1. The pressure of O_2 was approximately 2–5 × 10^{-6} mBar in the collision quadrupole housing, as measured with an ionization gauge. This value of the pressure in the housing allowed us to estimate the O_2 pressure in the collision cell (RF-only quadrupole ion guide) to be greater than 1 × 10^{-4} mBar using gas conductance calculations. The interaction region (collision quadrupole) has a length of 12.5 cm and 2 mm diameter entrance and exit apertures. Reactions corresponding to multiple collisions were observed. The kinetic energy of the precursor cluster ions ranged from 1 to 5 eV (lab coordinates). The precursor ion kinetic energy was optimized within this range to provide a maximum extent of reaction in terms of intensities of products. An energy analysis of the reactions is not strictly useful because multiple collision conditions were employed. The kinetic energy was measured by taking the differences between the DC potentials of the source and Q_1. The zero kinetic energy reference point was taken to be 99% attenuation of the ion beam. Other work has utilized 50%, 90%, and 99% attenuation of the main ion beam as a reference point.[29] Subsequent energy-resolved collision experiments on other metal cluster systems have utilized a retarding field analysis to determine the zero kinetic energy reference point and translational energy distribution of the ion beam.[30] These studies have shown that values obtained on our instrument using the different zero kinetic energy point criteria vary by up to 20%.

The titanium foil, titanium dioxide, and gases were obtained from commercial sources and used without further purification. The manufacturer's stated purity of the titanium foil was 99.98% (Alfa Products).

Results

Production of Titanium/Oxygen Cluster Ions. Oxygen-containing cluster ions were observed from both titanium dioxide and "pure" metal foil, when they were sputtered in a conventional FAB ion source. The titanium/oxygen cluster ions produced from sputtering the pure metal foil presumably arise from particle-induced desorption of chemisorbed oxygen on or in the metal foil. The foil was exposed to atmospheric oxygen and the background pressure in the ion source was about 1 × 10^{-6} mBar, corresponding to monolayer coverage by O_2 on the order of minutes. The formation of an oxide surface by dissociative chemisorption of oxygen on titanium is well-known and has been studied with use of secondary ion mass spectrometry (SIMS).[31]

Figure 1 displays the FAB mass spectrum obtained by sputtering titanium foil. The titanium/oxygen cluster ions are characterized by clusters of the form $[Ti_nO_{2n-\delta}]^+$, where n equals 1 to 8 and $\delta = 0$ to 4. Generally, oxygen-deficient ($\delta > 1$) cluster ions were more abundant than $\delta = 0$ or 1 clusters when sputtering the metal foil. This is due to a low concentration of oxygen in

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(25) The mass spectrometer was a VG 70-SEQ (VG Analytical Ltd., Wythenshawe, Manchester, UK) with EBQQ geometry (E = electrostatic sector (energy analyzer); B = magnetic sector (momentum analyzer); Q = quadrupole).

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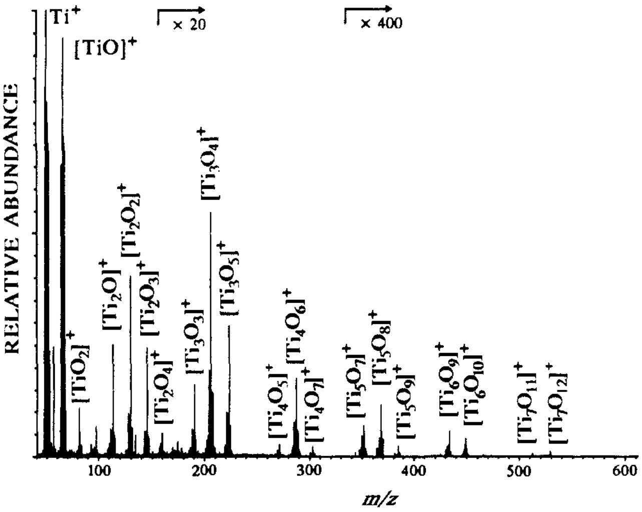

Figure 2. The FAB mass spectrum obtained from TiO_2 powder. The predominant cluster ions have the stoichiometry $[Ti_nO_{2n-\delta}]^+$ where δ is 1, 2, or 3.

or on the pure metal foil resulting in emission of primitive (less than stoichiometric) cluster oxides.

Figure 2 shows the FAB mass spectrum acquired by sputtering titanium dioxide powder. Three classes of cluster ions are abundantly produced. These classes have the empirical formulas $[Ti_nO_{2n-3}]^+$, $[Ti_nO_{2n-2}]^+$, and $[Ti_nO_{2n-1}]^+$. For n greater than 4, the $[Ti_nO_{2n-3}]^+$ and $[Ti_nO_{2n-2}]^+$ clusters predominate. The stoichiometries of the clusters correspond to nearly stoichiometric titanium(II) oxides. The tendency to observe more stoichiometrically deficient cluster ions as n increases may reflect the mechanism of the sputtering process. That is, larger cluster ions may be ejected intact by direct emission[32] from the metal oxide surface. If the assumption is made that statistically random bond cleavage occurs, a distribution of nearly stoichiometric products will be formed. However, energy deposited into the cluster ions during secondary ion formation can lead to unimolecular dissociation and hence formation of stoichiometrically deficient clusters. On the other hand, it is possible that the cluster ions are being formed by recombination within the selvedge region.[33] In this case, cluster ions may be produced that are stoichiometrically equivalent. To examine the mechanism for formation of the cluster ions, the oxidation and fragmentation of the cluster ions can be studied in the gas phase.

Titanium/oxygen cluster ions were formed by sputtering titanium foil in the HPFAB ion source. Sputtered bare metal and metal/oxygen cluster ions and neutrals react with O_2. At lower ion source pressures (less than 0.15 mBar) of O_2, the HPFAB mass spectrum was similar to the FAB mass spectrum of TiO_2 (Figure 2), producing abundant $[Ti_nO_{2n-2}]^+$ and $[Ti_nO_{2n-1}]^+$ clusters. As the pressure of O_2 was increased in the HPFAB ion source, the $[Ti_nO_{2n-2}]^+$ clusters became less abundant and the $[Ti_nO_{2n-1}]^+$ clusters predominated. Figure 3 shows the HPFAB mass spectrum acquired at an O_2 pressure of 0.25 mBar. The only cluster ions observed for n greater than 5 correspond to the series $[Ti_nO_{2n-1}]^+$. In contrast to the cobalt/oxygen cluster ions,[18] stoichiometrically equivalent $[(TiO_2)_n]^+$ clusters were not abundant and were not formed for $n > 3$. More highly oxygenated cluster ions (i.e. $[Ti_nO_{2n+1}]^+$ for $n > 2$) were not observed within the detection limits of our experiment.

Collision-Induced Dissociation of Titanium/Oxygen Cluster Ions. The products generated by collision-induced dissociation of titanium/oxygen cluster ions are listed in Table I. The titanium/oxygen cluster ions were produced by the three different methods detailed above: (i) sputtering Ti foil with use of FAB; (ii) sputtering TiO_2 with use of FAB; and (iii) sputtering Ti foil in the presence of O_2(g) under HPFAB conditions. The collision spectra of cluster ions produced with use of FAB and HPFAB ionization were acquired under the same instrumental conditions with the exception of oxygen as a reagent/buffer gas in the HPFAB experiment. Thus, any differences in the CID spectra are due to differences during ionization, such as isomer formation or internal energy differences in the cluster ions.

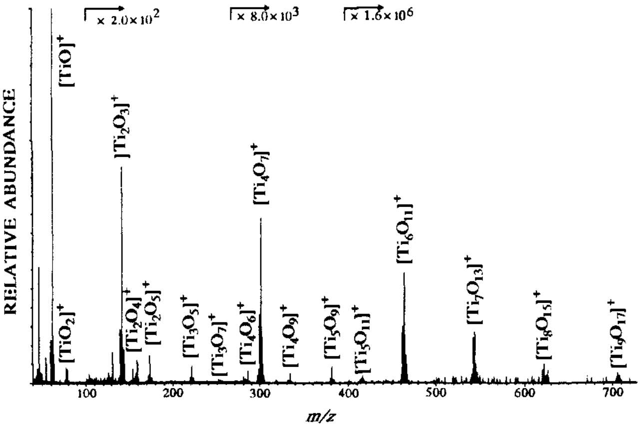

Figure 3. The HPFAB mass spectrum of Ti foil employing O_2 as a bath/reagent gas. The cluster ions have the stoichiometry $[Ti_nO_{2n-1}]^+$.

The titanium/oxygen cluster ions formed by the three different methods exhibit similar relative abundances of fragment ions especially for $\delta = 1$ or 2, with few exceptions (listed in Table I). The $[Ti_nO_{2n-1}]^+$ ($\delta = 1$) clusters produced by the different processes have similar low-energy CID spectra. The $\delta = 1$ cluster ions fragment to form $[Ti_{n-x}O_{2n-2x-1}]^+$ ($\delta = 1$) from the losses of $(TiO_2)_x$ where $x = 1$–3; the $[TiO]^+$ ion also corresponds to $\delta = 1$. In comparison with the $\delta = 1$ cluster ions, the $[Ti_nO_{2n-2}]^+$ ($\delta = 2$) clusters fragment to form abundant $[Ti_{n-1}O_{2n-3}]^+$ ($\delta = 1$) clusters via the loss of TiO. For $\delta = 2$ and $n = 3$, the loss of TiO_2 was also observed. In fact for $n = 4$, it is the most abundant fragment. Thus, the CID results correlate with the HPFAB results in that the predominant cluster ions or fragments that are formed correspond to $\delta = 1$. This indicates the stability or preferred formation of this series of cluster positive ions.

Some of the ions produced in the HPFAB source show different CID fragmentations. In particular, the loss of 2O from $[Ti_2O_2]^+$ ($\delta = 2$) and $[Ti_3O_4]^+$ ($\delta = 1$) was observed. This suggests the presence of isomers with weakly or electrostatically bound dioxygen. The presence of an electrostatically bound cluster indicates that the ions that are formed are not hot. This suggests that metal/oxygen cluster ions formed in the HPFAB ion source are being cooled or thermalized by collisions. Previous work has shown that the internal energy of desorbed ions can be reduced with use of HPFAB by examining the extent of metastable dissociation.[22] However, for the larger metal/oxygen cluster ions, no significant metastable dissociation was observed. It is interesting to note that the only other cluster listed in Table I that fragments to lose oxygen is the $[Ti_2O_4]^+$ ($\delta = 0$) cluster, which fragments to lose an oxygen atom forming a $\delta = 1$ cluster. The $[Ti_2O_4]^+$ cluster also shows a difference in the CID spectra depending upon whether the cluster is formed by sputtering from Ti foil or TiO_2 powder. Other $\delta = 0$ cluster ions were not abundant enough to obtain their collision spectra.

Table II displays a summary of the neutral fragment losses from the $[Ti_nO_{2n-\delta}]^+$ clusters by collision-induced dissociation. The losses all correspond to TiO_y ($y = 0$–2) moieties, with few exceptions. In addition, as δ increases, y decreases (Table II). That is, as the cluster becomes more oxygen deficient, it is reflected in the fragmentation. The only other abundant losses corresponded to the loss of $(TiO_2)_x$ where $x = 2$ or 3. These fragments could correspond to multiple fragments, such as 2 or 3 TiO_2 units. The identities of the neutral fragments can only be inferred, but it is

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reasonable to assume that they correspond to intact moieties. The formation of several neutral fragments would presumably require substantially more energy, due to the cleavage of additional metal/oxygen bonds. We are currently studying energy-resolved fragmentations to confirm this hypothesis from the observation of thresholds for the onset of collision-induced dissociation processes.[34] In summary, the losses during CID of the $[Ti_nO_{2n-\delta}]^+$ clusters are quite simple and appear to correspond to small, intact TiO_y (y = 0–2) fragments.

Hyperthermic Reactions of Titanium/Oxygen Cluster Ions. The gas-phase reactions of titanium/oxygen cluster ions with O_2 in the RF-only quadrupole were also studied with use of the methodology described above. By studying the reactions of mass-selected ions in the quadrupole collision/reaction cell, the products of the cluster ion–molecule reactions can be confirmed and delineated with less ambiguity than for ions emitted from the HPFAB source. The reactions were observed to occur for a limited range of kinetic (collision) energy and oxygen gas pressure. The abundance of the products depends greatly upon the collisional energy: no oxygen adducts were observed when E_{lab} was greater than 5–10 eV. For exothermic reactions, the reaction cross section can decrease quite rapidly.[28,35] Multiple collision conditions were employed to determine the maximum extent of reaction. Further work is being continued to determine the energy and pressure dependence of the reactions.[34] However, even at a single collision energy, useful information about the gas-phase reactivity of the titanium/oxygen cluster ions can be obtained.

The hyperthermic reaction products of the cluster ions are tabulated in Table III. Most of the cluster ions react to add one or two oxygen atoms. For cluster ions with δ = 2–4, the predominant products correspond to $[Ti_nO_{2n-1}]^+$ (δ = 1) cluster ions. For cluster ions with $\delta < 1$, adduct formation is not abundant. The collision-induced reactions are similar to the results obtained with Ar as a collision gas.

Discussion

The process of cluster ion emission is not well understood. There are two general mechanisms that have been proposed for the mechanism of cluster ion formation from a surface during particle bombardment: direct emission[32] and recombination.[33] Recent experiments on the emission/reaction of metal halide cluster ions in the HPFAB technique have addressed themselves to the sputtering process.[36] In this latter study, the mechanism for the formation of cluster ions is still not clear, but it is believed to consist, in part, of fast atom beam assisted reactions between the buffer gas and sputtered species in the selvedge region. Evidence was presented that appears to support a mechanism that is intermediate between the direct emission model and the recombination mechanism. Thus, cluster ions can be emitted from the surface, but they are subject to modification via cluster ion–molecule reactions within the nominally-high-pressure region of the HPFAB ion source. This appears to be the case for the titanium/oxygen cluster ions that we observe.

The similarity between the FAB spectra of titanium metal foil and titanium dioxide under the dynamic (more than monolayer removal) sputtering conditions that we employ implies that the mass spectra may not reflect the surface structure. On the other hand, experiments in the HPFAB ion source and hyperthermic reaction indicate that cluster ion–molecule reactions play an important role in the formation and stability of the $[Ti_nO_{2n-\delta}]^+$ cluster ions that are observed.

A Model of Titanium/Oxygen Cluster Structures. Important questions to be asked are (1) what are the structures of the cluster ions, and (2) why is the formation of the δ = 1 series predominant? We have investigated structures of metal/oxygen clusters using a simple, pair-potential model.[18] The geometries were obtained by minimizing the total potential energy of the cluster. The energy was calculated as a pairwise sum of Coulombic interactions and Born–Mayer repulsions. The geometries were optimized with use of the potential function

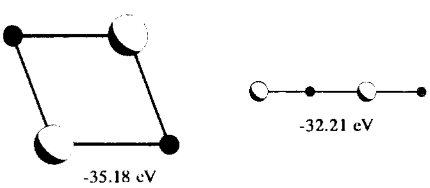

Figure 4. Structures of Ti_nO_{2n-2} clusters for n = 2 calculated with use of a pair-potential ionic model.

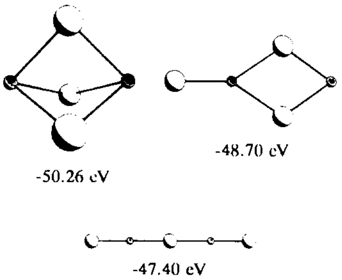

Figure 5. Structures of Ti_nO_{2n-1} clusters for n = 2 calculated with use of a pair-potential ionic model.

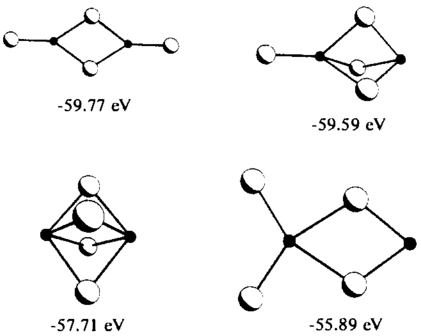

Figure 6. Structures of Ti_nO_{2n} clusters for n = 2 calculated with use of a pair-potential ionic model.

$$V_T = V_{MO}(r) + V_{MM}(r) + V_{OO}(r) \tag{1}$$

$$V_{ij}(r) = \frac{q_i q_j}{r_{ij}} + A \exp\left(\frac{r_{ij}}{\rho}\right) \tag{2}$$

where r_{ij} is the internuclear distance between each pair of atoms; q_M and q_o are the atomic charges determined by the stoichiometries of the observed cluster ions; and A and ρ are adjustable parameters obtained by requiring them to give the nearest-neighbor distance for the monomer and for the bulk solid. The values used for the calculations were A = 2605 $e^2 \cdot Å^{-1}$ and ρ = 0.1628 Å. For the titanium/oxygen clusters values of $q_M = +2\epsilon$ and $q_o = -\epsilon$, where ϵ = 1, were used to describe the clusters, given the observed stoichiometries from the experiment. A recent SCF-CI computation found that the bonding in the ground state for the TiO_2 molecule is partially ionic with a configuration of Ti^{2+} ($3d^2$) and O^- ($2p^5$).[37] This corroborates our use of the pair potential model to determine metal/oxygen cluster structures. The pair-potential model cannot account for metal–metal bonding. However, there is no evidence in the CID spectra of any fragments where there could be extensive M–M bonds.

Several low-energy isomers (local minima) are found by the model for each of the many homologues of the different classes. Structures found for the titanium/oxygen clusters are shown in

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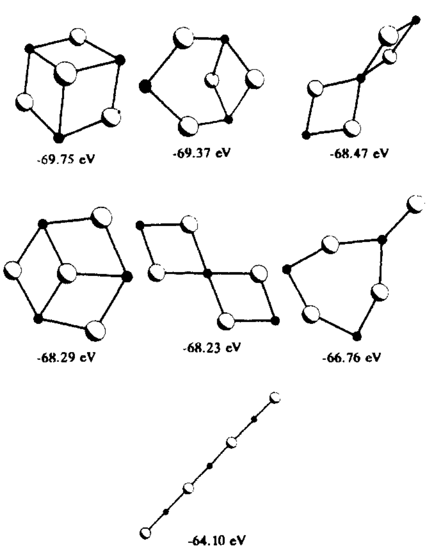

Figure 7. Structures of Ti_nO_{2n-2} clusters for $n = 3$ calculated with use of a pair-potential ionic model.

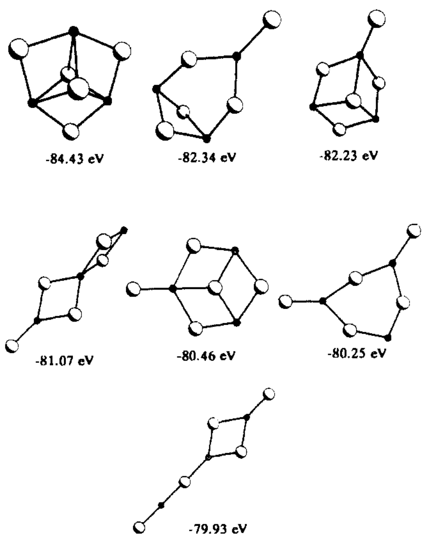

Figure 8. Structures of Ti_nO_{2n-1} clusters for $n = 3$ calculated with use of a pair-potential ionic model.

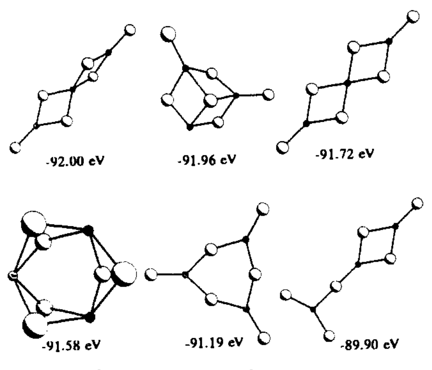

Figure 9. Structures of Ti_nO_{2n} clusters for $n = 3$ calculated with use of a pair-potential ionic model.

Figures 4–12. Homologues of each class retain some structural similarities. In particular, the lowest energy isomers of the δ = 1, 2 clusters are seen to be cubic or globular with no pendant or terminal atoms and multiple Ti–O bonds. The two classes of compounds with δ = 1, 2 were abundantly observed in the HPFAB spectra at lower O_2 pressures (less than 0.15 mBar) and in the FAB spectrum of TiO_2 (Figure 2). Dramatic structural differences are not evident between these two classes of compounds. On the other hand, the stoichiometrically equivalent δ = 0 clusters have pendant and terminal oxygen atoms in their structures, especially for the lowest energy isomers found. This is reflected in the CID fragmentations of the one δ = 0 cluster that was examined. The most abundant fragmentation of the $[Ti_2O_4]^+$ cluster formed in the HPFAB ion source was the loss of O. The loss of an O atom is also significant in the collision spectra of $[Ti_2O_4]^+$ formed from

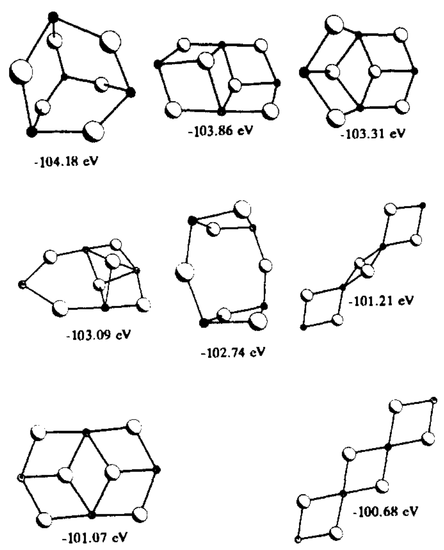

Figure 10. Structures of Ti_nO_{2n-2} clusters for $n = 4$ calculated with use of a pair-potential ionic model.

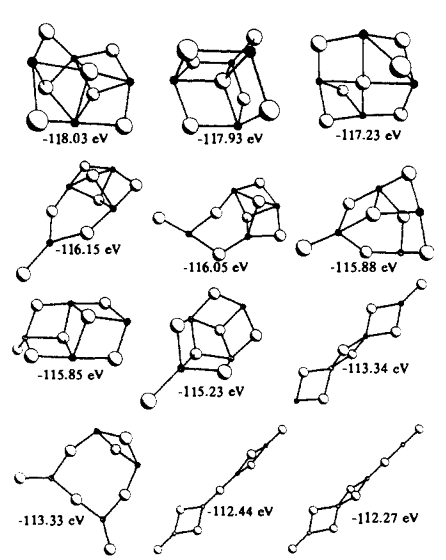

Figure 11. Structures of Ti_nO_{2n-1} clusters for $n = 4$ calculated with use of a pair-potential ionic model.

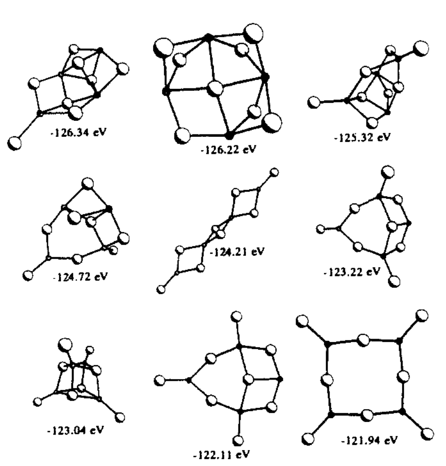

Figure 12. Structures of Ti_nO_{2n} clusters for $n = 4$ calculated with use of a pair-potential ionic model.

Table III. Hyperthermic Reaction Products of $[Ti_nO_{2n-\delta}]^+$ (δ = 0–4) Cluster Ions[a]

product			relative abundance[b]											
			$n = 2$					$n = 3$				$n = 4$		
stoichiometry	δ	K	$\delta = 0$[d]	$\delta = 1$	$\delta = 2$	$\delta = 3$	$\delta = 4$	$\delta = 1$	$\delta = 2$[e]	$\delta = 3$	$\delta = 4$	$\delta = 2$	$\delta = 3$	$\delta = 4$[f]
Ti^+	2	1	10	5		1	10							
$[TiO]^+$	1	3	100	100	95	100	100	50	30	90	100	8	100	86
$[TiO_2]^+$	0	5	8		37	6	1							
$[Ti_2O_2]^+$	2	2.5	15			2			10	15	22			
$[Ti_2O_3]^+$	1	3.5	30		100	8		23	34	100	30	5	78	100
$[Ti_2O_4]^+$	0	4.5		10					8					
$[Ti_2O_5]^+$	−1	5.5	5	25	70									
$[Ti_3O_4]^+$	2	3								14				8
$[Ti_3O_5]^+$	1	3.67							100	14		10	100	37
$[Ti_3O_7]^+$	−1	5						100						
$[Ti_4O_6]^+$	2	3.25											5	
$[Ti_4O_7]^+$	1	3.75										100	7	
$[Ti_4O_8]^+$	0	4.25										7		
$[Ti_4O_9]^+$	−1	4.75										18		

[a] Results for cluster ions formed by sputtering Ti foil in a conventional FAB ion source and using O_2 as a collision gas. [b] A value of 100 is given for the most abundant product ion. [c] The cluster fragment is given by $K = (q + 2m)/n$, where q (=1) is the charge and n and m are the number of metal and oxygen atoms. [d] The $[Ti_2O]^+$ (δ = 3, K = 1.5) product was observed to have an abundance of 8% of the most abundant product. [e] The $[Ti_3O_2]^+$ (δ = 4, K = 1.67) product was observed to have an abundance of 4% of the most abundant product. [f] The $[Ti_4O_4]^+$ (δ = 4, K = 2.25) product was observed to have an abundance of 5% of the most abundant product.

the other substrates (Table I). Higher order stoichiometric cluster ions were not abundant enough to be observed with CID. Thus, in comparison with the cobalt/oxygen clusters,[18] dramatic structural differences between the stoichiometric structures and the stoichiometrically deficient (metal or oxygen) clusters were found for the lowest energy isomers.

The δ = 0 cluster ions are significantly less abundant in the FAB or HPFAB mass spectra. In fact, they are only observed as products in the hyperthermic reactions of the $[Ti_2O_3]^+$, $[Ti_3O_4]^+$, and $[Ti_4O_6]^+$ clusters, forming $[Ti_2O_4]^+$ and $[Ti_4O_8]^+$ (Table III). These products could in fact correspond to ion–molecule complexes that are condensed adducts of dioxygen, particularly in the reaction of the $[Ti_4O_6]^+$ cluster. In fact, the most abundant hyperthermic product of the $[Ti_3O_5]^+$ clusters is the superoxygenated $[Ti_3O_7]^+$ cluster, which would correspond to a dioxygen adduct. For the $[Ti_3O_4]^+$ cluster, the formation of the $[Ti_2O_4]^+$ product would correspond to the loss of TiO_2 from a dioxygen adduct, an abundantly observed fragmentation in other cluster ions. For the reaction of $[Ti_2O_3]^+$, the formation of $[Ti_2O_4]^+$ would proceed with the loss of O from a cluster adduct. It is seen in Table I that $[Ti_2O_4]^+$ formed from the different substrates yields different fragment ions. The δ = 3 ion is the most abundant fragment when $[Ti_2O_4]^+$ is formed by sputtering Ti foil. It was not observed in either of the other two cases. This suggests the presence of different isomers of $[Ti_2O_4]^+$ clusters in our experiments. It should be noted that the fragmentation patterns could vary due to differences in internal energy of the cluster ions. It would be expected that cluster ions formed under HPFAB conditions would be cooler due to multiple thermalizing collisions. On the other hand, if the cluster ions are being formed by direct emission from surfaces, there is no apparent reason why $[Ti_2O_4]^+$ clusters emitted from an oxide surface should have a different internal energy distribution than $[Ti_2O_4]^+$ clusters emitted from a bulk oxide. Recombination to form the $[Ti_2O_4]^+$ cluster in the selvedge region might provide an explanation as different precursors might be expected to give rise to products with different internal energies. However, there is qualitatively good agreement between the abundances of the CID fragments of the other cluster ions where comparison can be made. Thus, the presence of isomers of $[Ti_2O_4]^+$ seems to be the most rational explanation. There is, in fact, one particular isomer shown in Figure 6 that is remarkably different, found at an energy of −57.71 eV. Such a structure would not be expected to readily lose 3 oxygen atoms. The loss of 3 oxygen atoms (or O and O_2) could more easily be accomplished from any of the other three isomers found, especially the lowest energy structure.

It might be argued that the low abundance of any $[Ti_nO_{2n}]^+$ clusters is due to the loss of pendant oxygen atoms in a rapid, facile decomposition within the FAB ion source. In fact, the instability (lack of abundance) of these cluster ions could be due to two unrelated reasons. Figure 13 plots the energy of the three lowest energy isomers found with use of the pair-potential model versus n for the titanium and cobalt/oxygen cluster structures. In each case, the clusters with the lowest energy per atom (energetically most stable) are found to consist of the most abundant clusters in the HPFAB mass spectra of the corresponding metals. That is, for the titanium system, δ = 1 cluster ions are the most abundant (Figure 3) and for the cobalt/oxygen system the δ = 0 cluster ions are the most abundant. The only exception to this analysis is the n = 2 clusters for titanium. In this case, the Ti_2O_4 cluster structures are found to be as stable as the Ti_2O_3 cluster structures. In fact, the $[Ti_2O_4]^+$ cluster was the only δ = 0 cluster that was abundant enough on which to perform CID. In contrast,

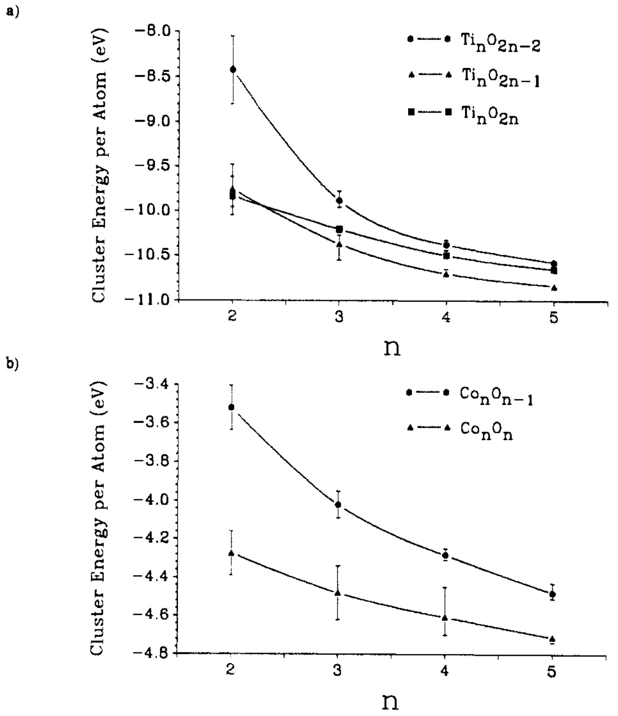

Figure 13. (a) A plot of the cluster energy per atom versus cluster number n found for Ti_nO_{2n-2}, Ti_nO_{2n-1}, and Ti_nO_{2n} cluster structures (Figures 4–12). (b) A plot of the cluster energy per atom versus cluster number n found for Co_nO_{n-1} and Co_nO_n cluster structures in ref 18. The data points are the average energy of the three lowest energy isomers found, listed in Table IV. The limits correspond to the range of energies for the isomers. The clusters with the lowest energy per atom are found to be the Ti_nO_{2n-1} series and the Co_nO_n series.

Table IV. Energy (eV) per Atom for the Three Lowest Energy Cluster Structures Found

	$[Ti_nO_{2n-2}]^+$	$[Ti_nO_{2n-1}]^+$	$[Ti_nO_{2n}]^+$	$[Co_nO_{n-1}]^{+a}$	$[Co_nO_n]^{+a}$
$n = 2$	−8.80	−10.05	−9.96	−3.52	−4.39
	−8.05	−9.74	−9.93		−4.16
		−9.48	−9.62		
$n = 3$	−9.96	−10.55	−10.22	−4.09	−4.62
	−9.91	−10.29	−10.21	−3.95	−4.34
	−9.78	−10.27	−10.19		
$n = 4$	−10.42	−10.73	−10.53	−4.31	−4.70
	−10.39	−10.72	−10.52	−4.29	−4.67
	−10.33	−10.65	−10.44	−4.25	−4.45
$n = 5$	−10.59	−10.86	−10.67	−4.51	−4.74
	−10.57	−10.83	−10.65	−4.50	−4.70
	−10.57	−10.82	−10.64	−4.43	−4.70

[a] Values taken from ref 18.

the $\delta = 2$ titanium cluster structures are found to be less stable than the $\delta = 0, 1$ cluster structures. Yet, they are observed in significant abundance in the FAB mass spectra of titanium foil and TiO_2. Under the oxidizing conditions of the HPFAB ion source, where cluster ion–molecule reactions can occur, the only cluster ions observed in significant abundance are the $\delta = 1$ cluster ions. This suggests that the cluster ions are formed by direct emission of cluster fragments from the oxide surfaces,[32] via a statistical distribution of Ti–O bonds being broken in which the cluster ions are somewhat indicative of the general nature of the surface. It is possible that the $\delta = 2$ cluster ions arise from rapid decompositions of larger cluster ions. This is seen in the fragmentations listed in Table I. The $[Ti_3O_4]^+$ and $[Ti_2O_2]^+$ fragments are observed to be abundant fragments from cluster ions where $\delta \geq 2$. In addition, the lowest energy structures in Figures 4 and 7 consist of structures that are the sides of a cube. Multiple bonds would be required to be broken to fragment into smaller cluster ions. If larger, primitive ($\delta \geq 2$) cluster ions are formed by direct emission and do fragment, they would be expected to produce the $\delta = 2$ cluster ions, as is observed during CID.

The $\delta = 0$ cluster ions may be less abundant for another simple reason. The $\delta = 0$ and ($\delta = -1$) cluster ions are observed in the hyperthermic reactions in Q_1. Yet they are not abundant from reactions in the HPFAB ion source. In the latter, a significant number of collisions (with oxygen and other species) occur. As the structures in Figures 6, 9, and 12 indicate, the clusters may have pendant oxygen atoms that can be removed by collisional activation within the ion source. These dissociations may be assisted by electronic effects. In fact, if one considers the cluster fragment valence K (listed in Table III)[38,39] for the cluster ions, the value of K for $\delta \leq 0$ is greater than 4. The calculation of cluster fragment valence assumes totally ionic bonding. Titanium has only four valence electrons ($[Ar]3d^24s^2$). Thus, to form a $\delta = 0$ cluster positive ion with Ti(IV), a valence electron needs to be removed from an oxygen. This suggests that if the bonding in the clusters is purely ionic, the ionization potential of these clusters would be large. Thus, the ionization potential of the $\delta = 0$ clusters may be determining the lack of abundance of any positive ions. Charge exchange reactions in the HPFAB ion source have been observed.[22] Abundant neutral species are formed during the sputtering process. Thus, cluster ions with a higher ionization potential could undergo charge exchange with neutral clusters having a lower ionization potential, such as might be expected for $\delta \geq 1$ clusters where the cluster fragment valence of the ion is less than 4. If ionization potential is the prime reason for lack of abundance, neutral clusters ($K = 4$) or negative ion clusters ($K < 4$) corresponding to $\delta = 0$ would be expected to be abundant. Our instrument is not sensitive to the detection of negative ions and we have no method for detecting neutral clusters other than by post-ionization, forming positive ions.

Conclusions

It might be expected that differences in reactivity between the $\delta = 0$ and the $\delta = 1, 2$ cluster ions will be found, as has been observed for the cobalt oxides.[19] These differences will not be based upon the reactivity of the metal atom but instead may reflect the ability of the $\delta = 0$ cluster ions to donate an oxygen atom or oxidize simple organic substrates. However, such further studies are beyond the scope of this work and require an abundance of the $\delta = 0$ cluster ions. The ionization potential of the $\delta = 0$ clusters or their geometric structures may account for their lack of abundance. In fact, the most abundant cluster produced with use of HPFAB corresponded to $\delta = 1$. It is interesting to note that this stoichiometry corresponds to a stable phase for bulk titanium oxide.[40-42]

An elementary pair-potential ionic model was used to calculate geometric structures for titanium/oxygen clusters. The observed stoichiometries of the clusters provided the basis for calculating the geometric structures. Several low-energy isomer structures were found for each cluster. Remarkably, the calculated structures exhibit edges and faces having the same stoichiometries as observed CID fragments. Calculated structures correlate with observed fragmentations of the metal/oxygen cluster ions. Titanium/oxygen cluster ions were observed to lose TiO or TiO_2 units. This contrasts with cobalt/oxygen cluster ions, which lose Co or CoO units.[18] Similar analyses and conclusions were made for $[M(MO)_x]^+$ and $[(MO)_x]^+$ (M = Fe, Co) cluster ions.[18,43] Future experiments will study the energy dependence of the oxygenation reactions of metal cluster ions with use of energy-resolved collision spectrometry.

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