Characterization of $Ti_6O_4(O_2C_4H_5)_8(OCH_2CH_3)_8$ by Electrospray Time of Flight Mass Spectrometry

Gregory A. Khitrov and Geoffrey F. Strouse
Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California, USA

Jean-Jacques Gaumet
Laboratoire de Spectrometrie de Masse et Chimie Laser, Universite de Metz, Metz, France

A titanium oxide molecular cluster prepared by hydrolysis of titanium tetraethoxide in the presence of methacrylic acid, can be characterized by electrospray time of flight mass spectrometry (ESMS-TOF). The chemistry of such systems is not well known and ESMS is a powerful technique for studying the reactions of clusters in solution. The fingerprint of the cluster fragmentation suggests formation of Ti_xO_y core fragments that represent commonly observed structural constructs in bulk titanium oxide metallates. The fragmentation steps provide insight into the hydrolytic conversion of this molecular sol gel intermediate into bulk TiO_2. While MS has been applied to the study of metal alkoxide hydrolysis mechanisms, mass spectra of isolated individual titanium oxide clusters have not previously been reported. (J Am Soc Mass Spectrom 2004, 15, 260–267) © 2004 American Society for Mass Spectrometry

Mass spectrometry is a unique analytical tool that allows the determination of the exact mass of molecular and nano sized biological, organic, and inorganic species [1–11]. In polymeric systems, MS techniques have been shown to provide accurate estimates of the average size and polydispersity. Continuing advances in ion source and mass analyzer technologies have resulted in the characterization of progressively larger species [5, 6, 8]. In particular, the use of the electrospray ionization (ESI) method for inorganic-organic hybrid materials has allowed for the mass spectral analysis of ions from the liquid phase with minimal fragmentation [11]. Coupling ESI with the use of tandem MS (MS/MS) is of even greater usefulness for the characterization of complicated chemical systems. The technique allows for the isolation of a single ion from an analyte mixture and the systematic degradation of this ion to establish its composition. In this way relationships between chemical species detected by MS may be established. In fact, MS analysis of metal chalcogenide clusters up to 1.2 nm has suggested that cluster fragmentation occurs along pseudo-lattice planes in such materials [9].

In this study, we report the ESMS and MS/MS characterization of the $[Ti_6O_4(EtO)_8(McO)_8]$ cluster (Figure 1) where EtO and McO denote ethoxide and methacrylate ligands, respectively. Discrete $[Ti_xO_yL_z]$ clusters are stable materials, consisting of a titanium oxide core surrounded by alkoxy or carboxylic acid ligands, that are important intermediates in the conversion of $Ti(OR)_4$ precursors to TiO_2 glasses and sol-gel materials by either acid or base catalyzed hydrolysis [12–16]. These clusters are obtained by in situ hydrolysis of $Ti(OR)_4$ in the presence of carboxylic acid. The bulky carboxylate ligands stabilize small titanium oxide clusters and prevent the formation of bulk TiO_2. Fragmentation analysis by MS/MS indicates formation of a family of species related to titanium oxide architectures commonly observed in bulk lattices. This suggests a surprising level of insight into structure stability can be gained by inspection of the fragmentation pattern in inorganic clusters. These clusters are potentially useful as building blocks in hybrid materials as it is possible to incorporate the organic capping groups into a polymer network while maintaining the integrity of the core [12–15]. While XRD, NMR, and spectroscopic studies exist, there are no published reports of a MS characterization of a discrete cluster with a Ti_xO_y core.
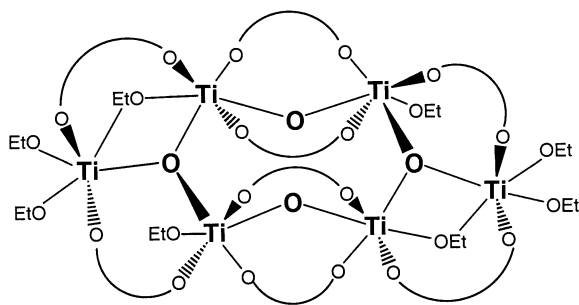
Experimental

$[Ti_6O_4(EtO)_8(McO)_8]$ clusters were synthesized as reported elsewhere [16]. They were kindly provided by Professor Ulrich Schubert. The clusters were stored in a nitrogen filled drybox to minimize hydrolysis. The
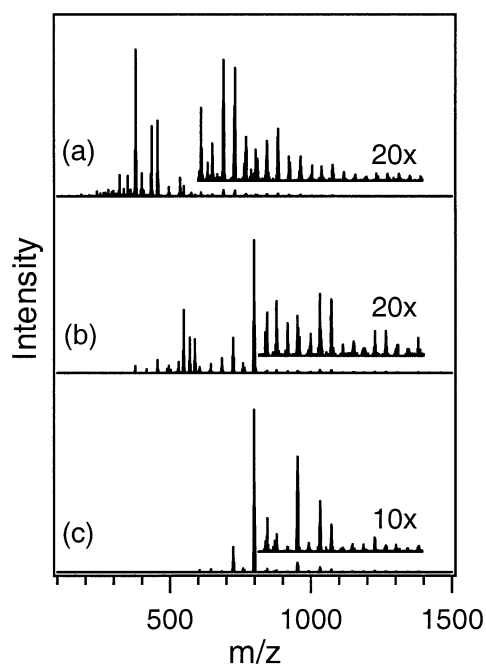
Figure 1. Structure of $Ti_6O_4(EtO)_8(McO)_8$. The methacrylate ligands are represented by curves for clarity.

Figure 2. Electrospray mass spectra of $Ti_6O_4(EtO)_8(McO)_8$ in toluene-ethanol using cone voltage settings: (**a**) +100, (**b**) +50, and (**c**) +30 V.

clusters were dissolved in dry toluene (Fisher, Pittsburgh, PA) to yield a 3 mM solution to which 100% ethanol (Fisher) was added to 17 volume %. The mass analysis was performed on a Waters (Milford, MA), QTOF2 mass spectrometer equipped with Quadrupole and time of flight (TOF) analyzers, as well as a hexapole collision cell. The sample solution was introduced by a Harvard syringe pump coupled to an infusion electrospray source. Block and desolvation temperatures were set to 120 and 150 °C, respectively. Cone voltage was varied between +30 and +100 V. Nitrogen was used as the nebulizing and desolvation gas, while argon was used as the collision gas. All gases were purchased from Air Liquide (Santa Barbara, CA) and were UHP grade. MS/MS was performed by setting the quadrupole analyzer to only pass ions of a specific m/z value, subjecting the ion to high energy collisions with argon atoms in the collision cell, and using the TOF analyzer to study the products of degradation as the collision voltage was increased. Collision voltage was varied between +10 and +80 V depending on the ion being analyzed. At least 100 scans were averaged, and smoothed for each mass spectrum presented. All peaks with a relative intensity of 3% of the maximum or higher were assigned to molecular species. All assigned peaks in the presented mass spectra were identified by the most abundant isotope (^{48}Ti, 73.8% abundance). Mass analysis and isotope modeling were performed on software provided by Micromass Inc. The instrument was externally calibrated with a standard mixture of NaI and CsI.

Results/Discussion

Figure 2 presents the positive ion mass spectrum of the $[Ti_6O_4(EtO)_8(McO)_8]$ parent cluster dissolved in dry toluene containing 17% ethanol by volume, collected with cone voltage settings of +30, +50 and +100 V. The significant observed mass peaks, their relative intensities, and the chemical species to which they were assigned appear in Table 1. The fragmentation of the parent cluster can be described as a series of substitutions of methacrylate by ethoxy ligands (Δm 40 Da); elimination of ethyl ether (Δm 74 Da); and loss of $[TiO(EtO)_2]$, $[TiO(McO)_2]$, and $[Ti(EtO)_4]$ fragments

(Δm 154, 234, 228 Da), which give rise to nine fragment families (A)–(I). In addition, fragmentation that results in a 28 Da mass change was observed which is either the result of hydrolysis, or ethylene elimination by the ethoxy ligands. Many of these processes, e.g., ligand exchange, ligand hydrolysis, and ether elimination have been previously observed in the solution chemistry of titanium oxide clusters capped with alkoxy and carboxylate ligands [14, 17–19]. The fragment family hierarchy is presented as a flowchart for ease of identification in Figure 3 with the schematic drawings of probable core structures of the nine cluster families shown in Figure 4. The structures adequately account for both the core atoms and the organic ligands in the assigned formulae of the MS species. While the structures of the fragment clusters could not be determined, clusters with identical core stoichiometries have been previously observed as intermediates and products of hydrolysis and ligand exchange reactions of titanium alkoxide precursors [20–29]. Furthermore, DFT calculations on unpassivated Ti oxide clusters reveal similar structures are thermodynamically stable, although cyclic forms are more stable than the acyclic structures represented in Figure 4 for systems without alkoxy stabilizing groups [30, 31]. These fragments may be important in the hydrolytic formation of TiO_2 sol gel materials.

The production of positively charged species appears to occur exclusively by loss of the negatively charged ethoxy or methacrylate ligands (Δm 45 or 85). None of the MS features were assigned to species formed by proton or metal ion addition as has been observed in ESI spectra of other metallate species. This

Table 1. Peak assignments for $Ti_6O_4(McO)_8(EtO)_8$ ESMS fragmentation products

| Core	Peak assignment	Normalized peak intensity			m/z Expt.	m/z Calc.
		30 V	50 V	100 V	(Da)	(Da)
A	$[Ti_5O_3(EtO)_9(McO)_4]^+$	3	—	—	1033.0	1033.20
	$[Ti_5O_3(EtO)_{11}(McO)_2]^+$	6	—	—	953.1	953.16
B	$[Ti_4O_2(EtO)_9(McO)_2]^+$	100	100	—	799.1	799.17
	$[Ti_4O_2(EtO)_{10}(McO)]^+$	—	7	—	759.1	759.15
C	$[Ti_4O_3(EtO)_6(McO)_3]^+$	—	5	—	765.1	765.07
	$[Ti_4O_3(EtO)_7(McO)_2]^+$	14	26	—	725.1	725.05
	$[Ti_4O_3(EtO)_8(McO)]^+$	—	10	—	685.1	685.03
	$[Ti_4O_3(EtO)(McO)_2]^+$	—	7	—	645.1	645.01
D	$[Ti_3O(EtO)_8(McO)]^+$	—	4	—	605.1	605.17
E	$[Ti_3O_2(EtO)_5(McO)_2]^+$	—	23	—	571.0	571.06
	$[Ti_3O_2(EtO)_6(McO)]^+$	—	8	—	531.1	531.04
	$[Ti_3O_2(EtO)_7]^+$	—	3	—	491.1	491.02
E2	$[Ti_3O_2(EtO)_5(McO)_2(H_2O)]^+$	—	24	—	589.1	589.08
	$[Ti_3O_2(EtO)_6(McO)(H_2O)]^+$	—	43	7	549.1	549.06
F	$[Ti_3O_3(EtO)(McO)_4]^+$	—	—	3	576.9	576.98
	$[Ti_3O_3(EtO)_2(McO)_3]^+$	—	—	13	536.9	536.96
	$[Ti_3O_3(EtO)_3(McO)_2]^+$	—	5	7	497.0	496.94
	$[Ti_3O_3(EtO)_4(McO)]^+$	—	8	51	457.0	456.92
	$[Ti_3O_3(EtO)_5]^+$	—	3	—	417.0	416.90
F2	$[Ti_3O_3(EtO)_5(H_2O)]^+$	—	—	46	435.0	434.92
	$[Ti_3O_3(EtO)_4(OH)(H_2O)]^+$	—	—	4	407.0	406.86
G	$[Ti_2O(EtO)_4(McO)]^+$	—	4	—[a]	377.1	377.06
	$[Ti_2O(EtO)_5]^+$	—	—	4	337.1	337.04
H	$[Ti_2O_2(McO)_3]^+$	—	—	N/A	383.0	382.98
	$[Ti_2O_2(EtO)(McO)_2]^+$	—	—	N/A	343.0	342.96
	$[Ti_2O_2(EtO)_2(McO)]^+$	—	—	N/A	303.0	302.94
	$[Ti_2O_2(EtO)_3]^+$	—	—	N/A	263.0	262.92
H2	$[Ti_2O_2(McO)_3(H_2O)]^+$	—	—	15	400.9	400.99
	$[Ti_2O_2(EtO)(McO)_2(H_2O)]^+$	—	—	5	360.9	360.97
	$[Ti_2O_2(EtO)_2(McO)(H_2O)]^+$	—	—	14	321.0	320.95
	$[Ti_2O_2(EtO)_3(H_2O)]^+$	—	—	4	281.0	280.93
H3	$[Ti_2O_2(EtO)(McO)_3(H_2O)_2]^+$	—	—	100	378.9	378.99
	$[Ti_2O_2(OH)(McO)_3(H_2O)_2]^+$	—	—	13	350.9	350.93
	$[Ti_2O_2(EtO)_3(H_2O)_2]^+$	—	—	3	299.0	298.94
I	$[Ti_4O_4(EtO)_3(McO)_4]^+$	—	—	4	730.9	730.97
	$[Ti_4O_4(EtO)_4(McO)_3]^+$	—	—	5	690.9	690.95
	$[Ti_4O_4(EtO)_6(McO)]^+$	—	—	3	611.0	610.91

[a]Possibly obscured by isotope pattern of m/z 379 species.

could be the result of positive ion scavenging by free ethoxy and methacrylate ions in solution. All the members of a fragment family possess the same titanium oxide core and are produced either by fragmentation of the same larger cluster, or from another family member by ligand exchange. Examination of MS/MS data on members within the same family found that the mass difference between principal fragmentation products was identical to the mass difference of the ions selected for controlled fragmentation. For example, in fragment family (A), MS/MS analysis of the two species yields fragments that are assignable to the mass difference arising from the replacement of the McO by an EtO ligand. The m/z 1033.0 ($[Ti_5O_3(EtO)_9(McO)_4]^+$) feature yields fragment products at m/z 805.1 and 765.1; while MS/MS of the species at m/z 953.1 ($[Ti_5O_3(EtO)_{11}(McO)_2]^+$) yields products at m/z 725.1 and 685.1. The mass difference is maintained in the fragmentation products, consistent with members existing within the same core family. Thus the larger members of family (C) would give rise to the larger fragments in family (F). Differences between the family members lie in the number of ethoxy, methacrylate, or hydroxy ligands that surround the core.

The mass spectrum obtained with the cone voltage set to +30 V represents the ions in solution with minimal fragmentation; lowering the cone voltage to +5 V and +15 V results only in a reduction of the signal levels. The cone voltage setting determines the energy with which the ions are accelerated into the analyzer, and therefore the likelihood of ion dissociation. The low cone voltage spectrum contains intense peaks at m/z 799.1 and 725.1, and much less intense peaks at m/z 953.1 and 1033.0. These peaks have been assigned to the species $[Ti_4O_2(EtO)_9(McO)_2]^+$ (B), species $[Ti_4O_3(EtO)_7(McO)_2]^+$ (C), and species $[Ti_5O_3(EtO)_{11}(McO)_2]^+$ and $[Ti_5O_3(EtO)_9(McO)_4]^+$ (A), respectively. Species in families (A) and (B)
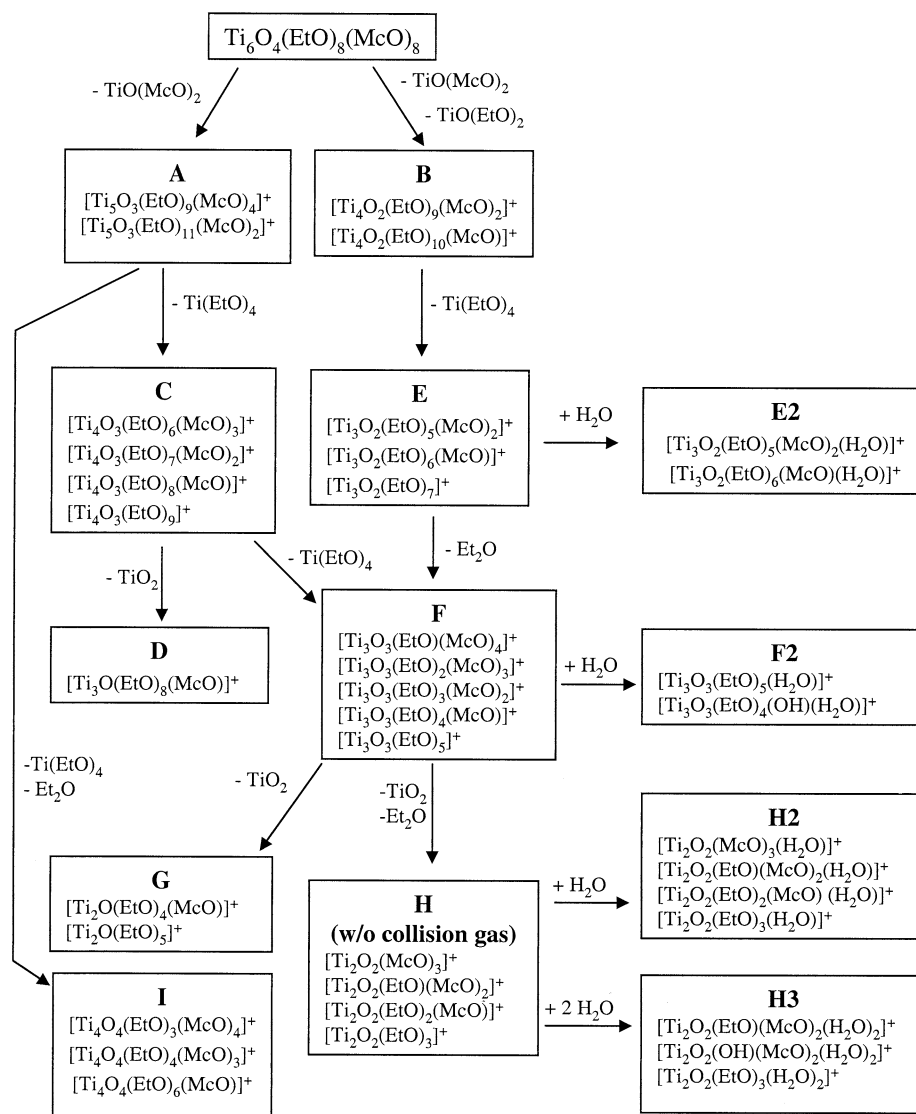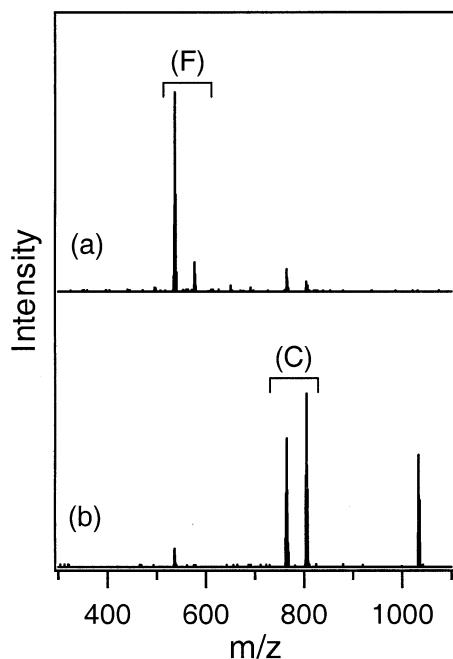
Figure 3. Proposed degradation pathway of the parent cluster it ethanol/toluene mixture. Abbreviations: EtO = ethoxy, McO = methacrylate, Et2O = diethyl ether.

represent the largest fragments of the parent cluster and their assigned chemical composition and structures are consistent with the loss of Ti-O units from the cluster core (Figure 4). No parent ion is observed for this material although a peak at m/z 1301 was observed when using a mass spectrometer equipped with a quadrupole analyzer that could only be assigned to the species $[Ti_6O_4(EtO)_6(McO)_8]^+$. This species could be produced by the elimination of an ethanol molecule from the parent cluster in addition to the loss of an ethoxy ligand to yield the positive charge. Alternatively, the species at m/z 1301 could be the result of a neutral $[Ti(EtO)_4]$ fragment addition to the species at m/z 1073 which is a member of the (A) family (see discussion at the end of the section). The (A) and (B) cores form independently since (B) does not appear in the tandem mass spectrum of (A) (Figure 5). The core stoichiometries of the two fami-
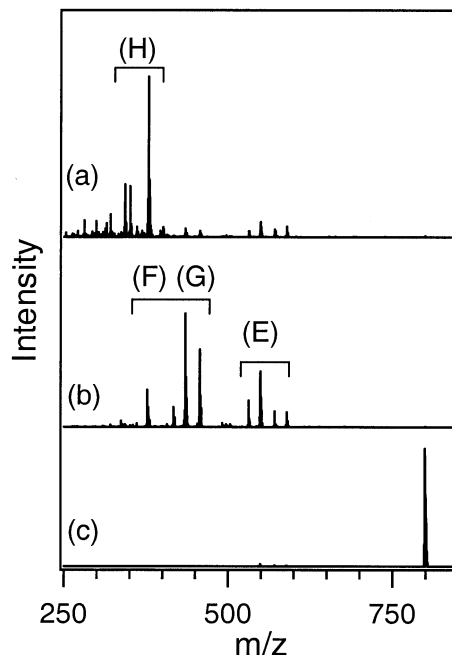
lies are consistent with the loss of a $[TiO(McO)_2]$ fragment from the parent cluster to yield (A) species, and the loss of an additional $[TiO(EtO)_2]$ fragment to yield (B) species. Both of these transformation processes were accompanied by the loss of a single methacrylate or ethoxy ligand to give the fragment a net positive charge, and the substitution of methacrylate by ethoxy groups. Ligand exchange by an ethoxy group for the bridging metacrylate at the Ti center is believed to initiate the degradation of the parent cluster by breaking a Ti–O bond, as was previously observed in the solution chemistry of similar clusters [32]. The lack of evidence for the conversion of a ligand oxygen to core oxygen atom by ether, ester, or anhydride elimination during the generation of core (A) and (B) species and the inability to assign the MS features to fragments with a different core stoichiometry suggest that the elimi-
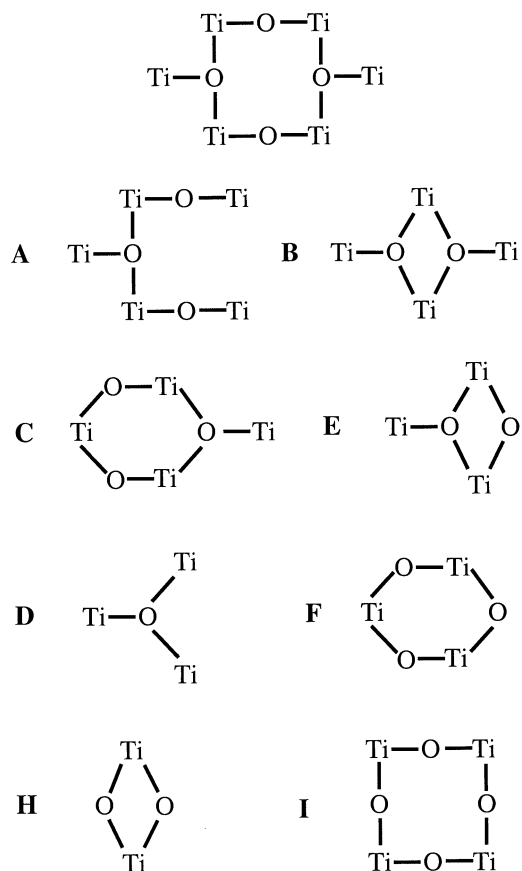
Figure 4. Schematic representations of the skeletal arrangements of the Ti and O atoms in the fragmentation product core structures.


Figure 6. Electrospray MS/MS spectra of the parent ion at *m/z* 799 using collision energy settings: (**a**) +60, (**b**) +40, (**c**) +10 V.

Figure 5. Electrospray MS/MS spectra of the parent ion at *m/z* 1033 using collision energy settings: (**a**) +40, (**b**) +20 V.

nated Ti-O species were part of the core. The Ti_4O_2 core structure of family (B) species [24, 25] has previously been observed in isolated products of the controlled titanium alkoxide hydrolysis. No reports of the isolation of species with the Ti_5O_3 structure were found. It is likely that this species is relatively unstable and is easily fragmented by coordinating ethoxy ligands in the analyte solution. This hypothesis is consistent with the relatively low intensity of the MS features attributed to this family, as well as the increase in intensity observed when lower concentrations of EtOH are used in the analyte solution. The appearance of the (C) species is consistent with a loss of a $[Ti(EtO)_4]$ fragment from the (A) cluster (Figures 3 and 5). $[Ti(OR)_4]$ elimination has previously been observed in the solution chemistry of $[Ti_xO_yL_z]$ type clusters [32] and in MS/MS studies of metal alkoxide clusters [33]. While clusters with the Ti_4O_3 core stoichiometry have not been isolated and characterized, we believe the ring structure shown in Figure 4 is plausible because ring structures have been assigned to the stoichiometries of most of the other stable fragments observed in these experiments.

Increasing the cone voltage to +50 V results in the formation of a (B) family species at *m/z* 759.1 which is consistent with the substitution of a methacrylate ligand on the 799.1 fragment by an ethoxy ligand. The fragmentation of (B) core species results in the appearance of peaks assigned to the (E) and (E2) fragment families (Figure 6). The stoichiometry of the family (E) species is consistent with the fragmentation of (B) to produce a family with the Ti_3O_2 core structure. Clusters with core (E) have been observed previously [29] and
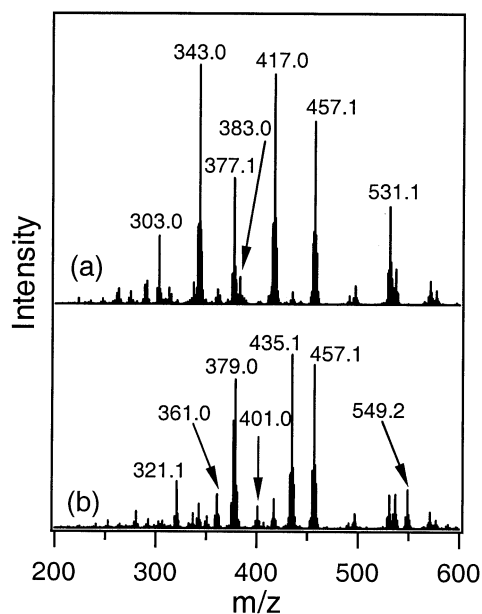
Figure 7. Features assigned to E, F, G, and H fragment families with the collision gas off (**a**), and E2, H2, and H3 families with the collision gas on (**b**). Spectra collected with the cone voltage set to +100 V.

the structure is shown in Figure 4. The structure and mass differences between the two families suggest that the (B) species undergo $[Ti(OEt)_4]$ elimination to yield (E) species at m/z 571.0, 531.1, and 491.1 with the general formula $[Ti_3O_2(EtO)_{5+n}(McO)_{2-n}]^+$ ($n = 0–2$). The (E2) fragment features appearing at m/z 589.1 and 549.1 were assigned to the general formula $[Ti_3O_2(EtO)_{5+n}(McO)_{2-n}(H_2O)]^+$ ($n = 0,1$), and share their core structure with the family (E) species. Family (E2) species are most likely the result of water addition to (E) species in the collision cell of the instrument. It is observed that (E2) features disappear and the intensities of the (E) species at m/z 571.0 and 531.1 increase when the collision gas is turned off (Figure 7). Furthermore, the attempt to use the Quadrupole analyzer to select the species at m/z 589.1 for MS/MS analysis resulted in no signal being observed even at the lowest collision energies, while a peak at m/z 589.1 was observed at low collision energies when the species at m/z 571.0 were selected for MS/MS analysis.

Increasing the cone voltage to +50 V also results in the increased fragmentation of the (A) family of clusters. The (A) fragments disappear, while the peaks assigned to the family (C) species increase in number and intensity. We see three additional family (C) species peaks appearing at m/z 765.1, 685.1, and 645.1. These peaks, along with the peak at m/z 725.1, were assigned to species with the general formula $[Ti_4O_3(EtO)_{6+n}(McO)_{3-n}]^+$ ($n = 0–3$). Because this formula has a limited number of methacrylate ligands, the peak at m/z 605.1 has been assigned to the species produced by TiO_2 elimination from the fragment at m/z 685.1 to yield $[Ti_3O(EtO)_8(McO)]^+$ as the lone represen-

tative of the (D) family. The structure of Ti_3O core clusters has been previously determined by several workers [20–22] and appears in Figure 4.

The features observed at m/z 497, 457, and 417 were assigned to the general formula $[Ti_3O_3(EtO)_{3+n}(McO)_{2-n}]^+$ ($n = 0–2$) and represent the (F) family of fragments. Unlike the fragment families discussed so far, members of the (F) family are observed in the tandem MS analyses of both family (C) and family (E) species. The formation of the family's Ti_3O_3 core is consistent with ethyl ether elimination from core (E) to yield an O bridge between two Ti atoms in Ti_3O_2 followed by a structural rearrangement to form the more stable ring structure (Figure 4) [23]. Conversely, core (F) could be produced from core (C) by the elimination of the pendant Ti atom in Ti_4O_3 as $[Ti(EtO)_4]$. Like the similarly structured family (C) species, the core (F) species at m/z 457.1 appear to undergo TiO_2 fragment elimination to produce a core (G) species at m/z 377.1 which was assigned to the formula of $[Ti_2O(EtO)_4(McO)]^+$. This elimination is probably a minor pathway in the fragmentation of (F) species as the peak has very low intensity. Another low intensity (G) peak appears at m/z 337.1 when the cone voltage is set to +100 V. It is interesting to point out that clusters with Ti_2O cores have been observed as unstable intermediates and possible building blocks of more complex titanium oxide species [23].

As the cone voltage is increased to +100 V, the MS features assigned to family (B), (C), (D), and (E) species disappear from the spectrum, while additional peaks assigned to species (F) appear at m/z 576.9 and 536.9, and are assigned to the general formula $[Ti_3O_3(EtO)_{1+n}(McO)_{4-n}]^+$ ($n = 0,1$). We also see the appearance of features at m/z 435.0 and 407.0 assigned to the (F2) fragment family. Like the features assigned to the (E2) family above, these features disappear when the collision gas is turned off indicating that they are the result of water addition in the collision cell. Based on this evidence, the m/z 435.0 species was assigned to the formula $[Ti_3O_3(EtO)_5(H_2O)]^+$. The low intensity peak at m/z 407.0 is probably the result of ethylene elimination from the species at m/z 435.0 in the high energy environment of the ion source [33].

The fragmentation of family (F) continues with the appearance of (H2) fragment family features at m/z 400.9, 360.9, 320.9, and 281.0 assigned to the general formula $[Ti_2O_2(EtO)_{0+n}(McO)_{3-n}(H_2O)]^+$ ($n = 0–3$). These features disappear when the collision gas is turned off allowing the observation of core (H) features at m/z 383.0, 343.0, 303.0, and 263.0 (Figure 7). These features were assigned to the general formula $[Ti_2O_2(EtO)_{0+n}(McO)_{3-n}]^+$ ($n = 0–3$). This core could be produced by the elimination of TiO_2 and ethyl ether, or the loss of a $[TiO(EtO)_2]$ fragment from (F) family species (Figure 4). It is possible that fragment family (G) is an intermediate in the (H) core formation. Additional spectral features assigned to species having the Ti_2O_2 core and assigned to the (H3) family were observed at

m/z 378.9, 350.9, and 299.0. The species at m/z 378.9 and 299.0 which may be the products of the addition of two water molecules to the species at 343.0 and 263.0, respectively. The species at 350.9 which could be the addition of two water molecules to the species $[Ti_3O_4(EtO)_2(OH)]^+$ which is the result of an ethylene elimination from the species at m/z 343.0.

We also observe the appearance of peaks at m/z 730.9, 690.9, and 611.0 (Table 1). These peaks were assigned to family (I) species having the general formula $[Ti_4O_4(EtO)_{3+n}(McO)_{4-n}]^+$ (n = 0,1,3). Stable species with Ti_4O_4 cores have previously been observed [26–28] and exhibit the ring structure shown in Figure 4. Very weak features assigned to family (I) fragments appear in the tandem MS spectra of family (A), and could be the result of $[Ti(EtO)_4]$ and ethyl ether elimination from family (A) clusters. Quite unexpectedly, family (I) species do not appear in the tandem MS of family (C) even though the latter would seem to be intermediates in their formation. Perhaps the ethyl ether elimination step cannot take place in the collision cell and only occurs in solution or at the ion source. Another possible assignment of the species at m/z 730.9, 690.9, and 611.0 is ligand exchange of ethoxy by methacrylate ligands (mass addition of m/z 40) to the (E) family of fragments. It is possible that at the high cone voltage, rapid ligand exchange may occur between the fragments in the source, although cluster fragmentation is expected to be the primary process observed at high cone voltage. Low intensity fragments that appear to be the result of this process can be observed if the higher m/z section of the +100 V data is magnified (Figure 2).

There is a possibility that the fragmentation pathway described above leads not to the structures shown in Figure 4 but to polymeric species that form by addition of neutral fragments ($[TiO_2]$, $[Et_2O]$, and $[Ti(EtO)_4]$) to small charged fragments of $Ti_6O_4(McO)_8(EtO)_8$ in solution. In this scenario, the cluster would quickly fragment in the coordinating solvent to form the (F) and (G) families of clusters which would gain the neutral fragments necessary to form species with core stoichiometries corresponding to all the larger cluster families. The formation of such polymer like species has previously been observed for titanium alkoxides as well as various polyoxometallate species in solution [18, 34, 35] and is very likely. These neutral adducts would then be progressively removed from the large species at higher cone voltages to give the appearance of large cluster degradation.

Conclusion

We have studied the fragmentation of the $Ti_6O_4(O_2C_4H_5)_8(OCH_2CH_3)_8$ molecular cluster in a mixture of toluene and ethanol by ESI-MS and MS/MS. We determined that the fragmentation products can be explained by the combination of pathways previously observed in solution and in the higher energy environment of the ESI source or TOF analyzer. A fragmentation mechanism for the cluster was proposed on the basis of the species observed in the MS and was found to be consistent with the previously reported structures and chemistry of the species involved.

Acknowledgments

References

1. Schalley, C. A. Molecular Recognition and Supramolecular Chemistry in the Gas Phase. *Mass Spectrom. Rev.* **2001,** *20,* 253–309.
2. Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. Applications of Electro-Spray Mass Spectrometry in Organometallic Chemistry. *Polyhedron* **1998,** *17,* 4291–4313.
3. Fenselau, C.; Demirev, P. A. Characterization of Intact Microorganisms by MALDI Mass Spectrometry. *Mass Spectrom. Rev.* **2001,** *20,* 157–171.
4. Godovac-Zimmermann, J.; Brown, L. R. Perspectives for Mass Spectrometry and Functional Proteomics. *Mass Spectrom. Rev.* **2001,** *20,* 1–57.
5. Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Verzmar, I.; Whetten, R. L. Properties of a Ubiquitous 29 kDa Au: SR Cluster Compound. *J. Phys. Chem. B* **2001,** *105,* 8785–8796.
6. Muddiman, D. C.; Null, A. P.; Hannis, J. C. Precise Mass Measurement of a Double-Stranded 500 Base-pair (309 kDa) Polymerase Chain Reaction Product by Negative Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Rapid Commun. Mass Spectrom.* **1999,** *13,* 1201–1204.
7. Bossio, R. E.; Callahan, S. D.; Stiegman, A. E.; Marshall, A. G. Complexation and Molecular Speciation in the Silica Sol-Gel Process Characterized by Electrospray Ionization Fourier Transform Ion-cyclotron Resonance Mass Spectrometry. *Chem. Mater.* **2001,** *13,* 2097–2102.
8. Peterson, J.; Allikmaa, V.; Subbi, J.; Pehk, T.; Lopp, M. Structural Deviations in Poly(amidoamine) Dendrimers: A MALDI-TOF MS Analysis. *Eur. Polym. J.* **2003,** *39,* 33–42.
9. Gaumet, J. J.; Khitrov, G. A.; Strouse, G. F. Mass Spectrometry Analysis of the 1.5 nm Sphaelerite-CdS Core of $[Cd_{32}S_{14}(SC_6H_5)_{36}$ · DMF$_4]$. *Nano. Lett.* **2002,** *2,* 375–379.
10. d'Avray, A. T. D.; Carpenter, E. E.; O'Connor, C. J.; Cole, R. B. *Eur. Mass Spectrom.* **1998,** *4,* 441–449.
11. Colton, R.; D'Agostino, A.; Traeger, J. C. Electrospray Mass Spectrometry Applied to Inorganic and Organometallic Chemistry. *Mass Spectrom. Rev.* **1995,** *14,* 79–106.
12. Moraru, B.; Husing, N.; Kickelbick, G.; Schubert, U.; Fratzl, P.; Peterlik, H. Inorganic–Organic Hybrid Polymers by Polymerization of Methacrylate- or Acrylate–Substituted Oxotitanium Clusters with Methyl Methacrylate or Methacrylic Acid. *Chem. Mater.* **2002,** *14,* 2732–2740.
13. Kickelbick, G.; Schubert, U. Inorganic Clusters in Organic Polymers and the Use of Polyfunctional Inorganic Compounds as Polymerization Initiators. *Monatsh. Chem.* **2001,** *132,* 13–30.
14. Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W. Dodecatitanates: A New Family of Stable Polyoxotitanates. *J. Am. Chem. Soc.* **1993,** *115,* 8469–8470.
15. Schubert, U. Polymers Reinforced by Covalently Bonded Inorganic Clusters. *Chem. Mater.* **2001,** *13,* 3487–3494.

16. Schubert, U.; Arpac, E.; Glaubitt, W.; Helmerich, A.; Chau, C. Primary Hydrolysis Products Of Methacrylate-Modified Titanium and Zirconium Alcoxides. *Chem. Mater.* **1992,** *4,* 291–295.

17. Soler-Illia, G. J. de A. A.; Scolan, E.; Louis, A.; Albouy, P. A.; Sanchez, C. Design of Meso-Structured Titanium Oxo Based Hybrid Organic-Inorganic Networks. *New J. Chem.* **2001,** *25,* 156–165.

18. Steunou, N.; Kickelbick, G.; Boubekeur, K.; Sanchez, C. A New Polyoxo-Alkoxo Titanium Cluster of the Keggin Family: Synthesis and Characterization by X-ray Diffraction and NMR Spectroscopy. *J. Chem. Soc. Dalton Trans.* **1999,** 3653–3655.

19. Lover, T.; Henderson, W.; Bowmaker, G. A.; Seakins, J. M.; Cooney, R. P. Electrospray Mass Spectrometry of Highly Moisture-Sensitive Metal Alkoxides. *J. Mater. Chem.* **1997,** *7,* 1553–1558.

20. Barkley, J. V.; Cannadine, J. C.; Hannaford, I.; Harding, M. M.; Steiner, A.; Tallon, J.; Whyman, R. Preparation and X-ray Crystallographic Characterization of the Trititanate [$Ti_3O(\mu$-$OPr^i)_3(OPr^i)_4\{Me_2C(O) CH = C(O)CH_2C(O)Me_2\}$], a Reaction Product of [$Ti(OPr^i)_4$] and Propan-2-one. *Chem. Commun.* **1997,** 1653–1654.

21. Mijatovic, I.; Kickelbick, G.; Puchberger, M.; Schubert, U. Preservation of the Cluster Core upon Formation of $Ti_3O(OPr^i)_8$ (benzoate)$_2$ from $Ti_3O(OR)_{10}$. *New J. Chem.* **2003,** *27,* 3–5.

22. Boyle, T. J.; Tyner, R. P.; Alam, T. M.; Scott, B. L.; Ziller, J. W.; Potter, B. G., Jr. Implications for the Thin-film Densification of TiO_2 from Carboxylic Acid-modified Titanium Alkoxides. Syntheses, Characterizations X-ray Structures of $Ti_3(\mu_3$-$O)(O_2CH)_2(ONep)_8$, $Ti_3(\mu_3$-$O)(O_2CMe)_2 (ONep)_8$, $Ti_6(\mu_3$-$O)_6(O_2CCHMe_2)_6(ONep)_6$, [$Ti(\mu$-$O_3CCMe_3)(ONep)_3]_2$, and $Ti_3(\mu_3$-$O) (O_2CCH_2CMe_3)(ONep)_8$ (ONep = $OCH_2 CMe_3$). *J. Am. Chem. Soc.* **1999,** *121,* 12104–12112.

23. Carofiglio, T.; Floriani, C.; Sgamellotti, A.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. Monocyclopentadienylchlorooxotitanium (IV) Dimers, Trimers, and Tetramers. *J. Chem. Soc. Dalton Trans.* **1992,** 1081–1087.

24. Moran, P. D.; Rickard, C. E. F.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L. X-ray Structure and Raman Spectrum of [$Ti_4(\mu_3$-$O)_2(\mu_2$-$O^iPr)_2(O^iPr)_8$ (acac)$_2$]: Presence of a $Ti_4(\mu_3$-$O)_2(\mu_2$-$O^iPr)_2$ Ladder-like Core. *Inorg. Chem.* **1998,** *37,* 1417–1419.

25. Boyle, T. J.; Alam, T. M.; Tafoya, C.; Scott, B. L. Formic Acid Modified $Ti(OCHMe_2)_4$. Syntheses, Characterization, and X-

ray Structures of $Ti_4(\mu_4$-$O)(\mu$-$O)(OFc)_2(\mu$-$OR)_4(OR)_6$ and $Ti_6(\mu_3$-$O)_6(OFc)_6(OR)_6$ (OFc = O_2CH; OR = $OCHMe_2$). *Inorg. Chem.* **1998,** *37,* 5588–5594.

26. Troyanov, S. I.; Gorbenko, O. Y. Crystal and Molecular Structure of Cyclo-tetrakis [μ-oxo-bis(2,2,6,6-Tetramethylheptan-3,5-Dionate)Titanium(IV)] Pentane Adduct. *Polyhedron* **1997,** *16,* 777–780.

27. Johnson, B. F. G.; Klunduk, M. C.; O'Connel, T. J.; McIntosh, C.; Ridland, J. The Compound [$Ti_4O_4\{OCH_2CH_2N (CH_3)_2\}_8$] Containing the New Ti_4O_4 Cluster Core. *J. Chem. Soc. Dalton Trans.* **2001,** 1553–1555.

28. Willey, G. R.; Palin, J.; Drew, M. G. B. Controlled Hydrolysis Reactions of Solvated [$TiCl_n$]$^{(4-n)+}$ Species. Crystal and Molecular Structures of [$Mg(MeCN)_6$] [$\{TiCl_4 (MeCN)\}_2(\mu$-$O)$] $\cdot$ 4MeCN and [$\{TiCl_2 (MeCN)_2(\mu$-$O)\}_4$] $\cdot$ 2MeCN. *J. Chem. Soc. Dalton Trans.* **1994,** 1799–1804.

29. Barrow, H.; Brown, D. A.; Alcock, N. W.; Errington, W.; Wallbridge, M. G. H. Titanium Oxo Carboxylate Compounds. Crystal and Molecular Structures of [$\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O$] and [$Ti_3Cl_3O_2 (O_2CEt)_5$] and an Unusual Quantitative Conversion of a Ti_2O to a Ti_3O_2 Oxo Derivative. *J. Chem. Soc. Dalton Trans.* **1994,** 3533–3538.

30. Albaret, T.; Finocchi, F.; Noguera, C. Ab Initio Simulation of Titanium Dioxide Clusters. *Appl. Surf. Sci.* **1999,** *144/145,* 672–676.

31. Yu, W.; Freas, R. B. Formation and Fragmentation of Gas-Phase Titanium/Oxygen Cluster Positive Ions. *J. Am. Chem. Soc.* **1990,** *112,* 7126–7133.

32. Mijatovic, I.; Kickelbick, G.; Schubert, U. Rearrangement of a Titanium Alcoxide Cluster upon Substitution of the Alcoxide Groups by Carboxylate Ligands—Synthesis of [$Ti_6O_4(OEt)_{14}(OOCPh)_2$] from [$Ti_7O_4 (OEt)_{20}$]. *Eur. J. Inorg. Chem.* **2001,** *8,* 1933–1935.

33. Zemski, K. A.; Castelman, A. W.; Thorn, D. L. Solution Phase Cationic Niobium and Tantalum Alkoxide Clusters: Insights into Formation and Structure. *J. Phys. Chem. A* **2001,** *105,* 4633–4639.

34. Sahureka, F.; Burns, R. C.; von Nagy-Felsobuki, E. I. Electrospray Identification of New Polyoxochromate Species. *Inorg. Chim. Acta* **2002,** *332,* 7–17.

35. Deery, M. J.; Howarth, O. W.; Jennings, K. R. Application of Electrospray Ionization Mass Spectrometry to the Study of Dilute Aqueous Oligomeric Anions and their Reactions. *J. Chem. Soc. Dalton Trans.* **1997,** 4783–4788.