

## Intracluster Ion-Molecule Reactions within $\text{Ti}^+(\text{CH}_2\text{FCH}_2\text{OH})_n$ Clusters

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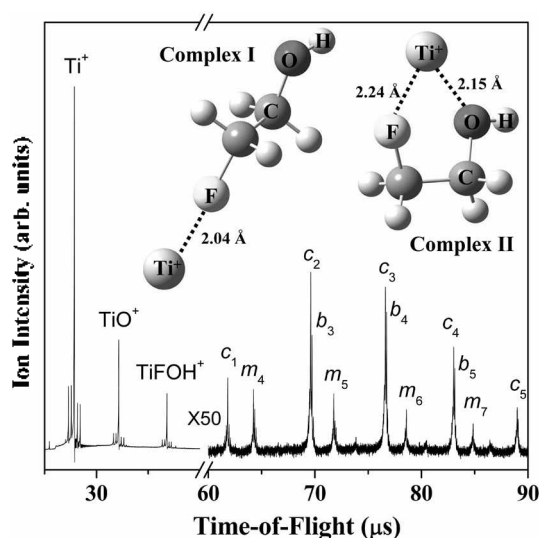
The importance of chemical reactions induced by interactions between transition metal ions and hydrocarbon molecules in a wide range of biological, chemical, and physical processes has prompted extensive studies aimed at elucidating the catalytic activities of transition metal ions.<sup>1</sup> The  $\text{Ti}^+$  ion activates C-C, C-H, and O-O bonds in specific gas-phase reactions.<sup>2</sup> Although the reactions of  $\text{Ti}^+$  with small molecules have been investigated in numerous works, few studies have examined the mechanism and energetics of the reactions of  $\text{Ti}^+$  with molecules possessing more than one functional group. Study of the specific chemical dynamics of reactions within cluster ions provides valuable information on the changes in the reaction pathways as a function of cluster size.<sup>3</sup>

In the present study, we investigated  $\text{Ti}^+(\text{CH}_2\text{FCH}_2\text{OH})_n$  heterocluster systems to search for new intracluster ion-molecule reactions occurring within the ionized clusters and to elucidate reactive pathways not ordinarily found in bimolecular ion-molecule collisions. The apparatus used in this work has been described previously.<sup>4</sup> Briefly, laser-ablated species containing  $\text{Ti}^+$  ions traversed perpendicular to a supersonic beam of  $\text{CH}_2\text{FCH}_2\text{OH}$  clusters 1 cm away

from a rotating target, where they reacted with the reactant clusters. The resulting ions were then analyzed by a reflectron time-of-flight mass spectrometer (RTOFMS). Figure 1 shows a typical TOF mass spectrum of the product species. In the low mass region, the reaction products consist of  $\text{TiO}^+$  ( $m/e = 64$ ) and  $\text{TiFOH}^+$  ( $m/e = 84$ ) formed from the ion-molecule reactions of  $\text{Ti}^+$  and 2-fluoroethanol (FE). The prominent peaks in the large mass region of the spectrum correspond to cluster ions with formulas  $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})(\text{FE})_n$  (denoted  $b_n$ ),  $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$  (denoted  $c_n$ ), and  $(\text{FE})_n\text{H}^+$  (denoted  $m_n$ ). The presence of  $(\text{FE})_n\text{H}^+$  cluster ions can be attributed to intracluster protonation of the parent  $(\text{FE})_n^+$  ions formed in the region where the laser-ablated plume and supersonic FE cluster beam intersect.

To interpret the reaction mechanism, we calculated the ground state structures and absolute energies of the  $\text{Ti}^+$ -FE complexes and related reaction products at the B3LYP/6-311++G(d,p) level using the Gaussian 03W package, which includes Becke's three parameter nonlocal hybrid exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr.<sup>5</sup> The optimized structures of the two  $\text{Ti}^+$ -FE isomers (referred to as I and II) are depicted in Figure 1. Complex I represents the case in which the  $\text{Ti}^+$  ion approaches to a distance of 2.04 Å from the F atom of the alkyl group, thereby activating the C-F bond. Complex II corresponds to the case in which  $\text{Ti}^+$  interacts with both the O and F atoms of FE, forming a complex containing a five-membered ring. Note that structure II is more stable than structure I by 28.6 kcal/mol, suggesting that complex II is the more favorable of the two structures in the experiments carried out in the present work. Moreover, since the  $\text{Ti}^+$  ion in complex II is closer to the O atom (2.15 Å) than the F atom (2.24 Å), rupture of the C-O and O-H bonds appears to be more facile than rupturing the C-F bond.

Scheme 1 provides a summary of the reaction pathways of  $\text{Ti}^+ + \text{FE}$ , along with the calculated reaction energies. The reaction pathways can be divided into two categories: (i) C-O bond activation and (ii) O-H bond activation.  $\text{Ti}^+$  insertion into the C-O bond of a FE molecule can lead to a  $[\text{HO-Ti-CH}_2\text{CH}_2\text{F}]$  intermediate. This intermediate could undergo  $\alpha$ -H atom transfer from the OH group to the  $\text{Ti}^+$  ion, followed by  $\text{CH}_3\text{CH}_2\text{F}$  elimination, to produce  $\text{TiO}^+$ . This mechanism is analogous to the  $\text{Ti}^+ + \text{H}_2\text{O} \rightarrow \text{TiO}^+ + \text{H}_2$  reaction, in which the dehydrogenation channel proceeds from a  $[\text{H-Ti-OH}]$  intermediate by a H migration from O to



**Figure 1.** Mass spectrum of the cluster ions produced by reactive collisions of laser-ablated  $\text{Ti}^+$  and 2-fluoroethanol (FE) clusters seeded in 1.7 atm Ar.  $b_n$ :  $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})(\text{FE})_n$ ;  $c_n$ :  $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$ ;  $m_n$ :  $(\text{FE})_n\text{H}^+$ . Ab initio calculations show the optimized ground-state structures for the two possible  $\text{Ti}^+$ -FE complexes.

