

Intracuster 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.¹ The Ti^+ ion activates C-C, C-H, and O-O bonds in specific gas-phase reactions.² Although the reactions of Ti^+ with small molecules have been investigated in numerous works, few studies have examined the mechanism and energetics of the reactions of 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.³

In the present study, we investigated $\text{Ti}^+(\text{CH}_2\text{FCH}_2\text{OH})_n$ heterocluster systems to search for new intracuster 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.⁴ Briefly, laser-ablated species containing 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 TiO^+ ($m/e = 64$) and TiFOH^+ ($m/e = 84$) formed from the ion-molecule reactions of 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 intracuster 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 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.⁵ The optimized structures of the two Ti^+ -FE isomers (referred to as I and II) are depicted in Figure 1. Complex I represents the case in which the 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 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 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. Ti^+ insertion into the C-O bond of a FE molecule can lead to a $[\text{HO-Ti}^+-\text{CH}_2\text{CH}_2\text{F}]$ intermediate. This intermediate could undergo α -H atom transfer from the OH group to the Ti^+ ion, followed by $\text{CH}_3\text{CH}_2\text{F}$ elimination, to produce 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 $[\text{H-Ti}^+-\text{OH}]$ intermediate by a H migration from O to

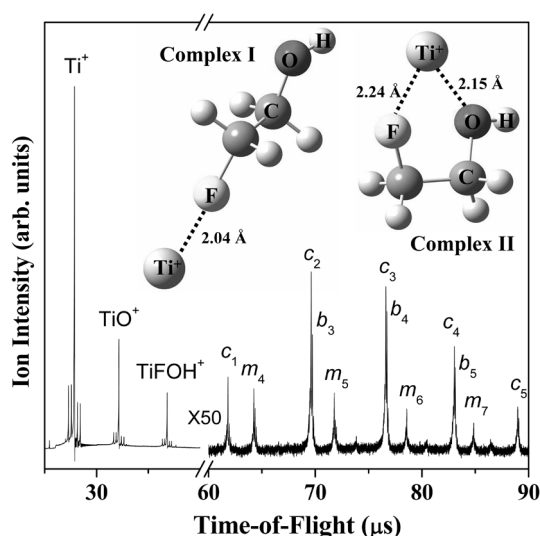
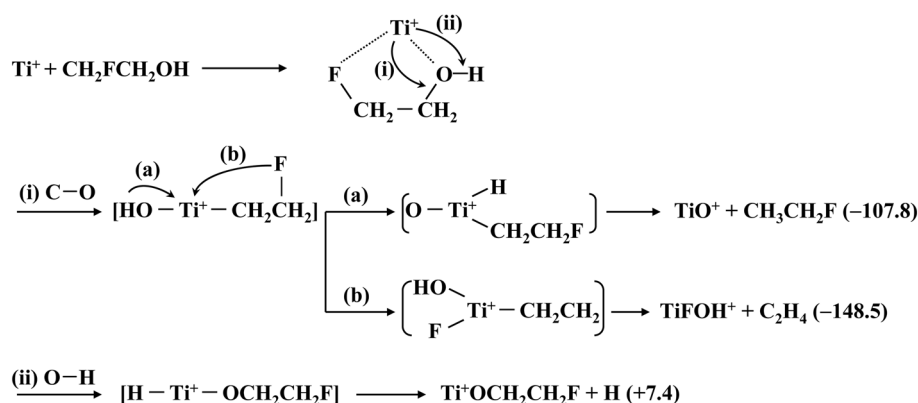


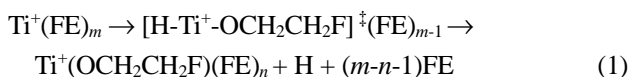
Figure 1. Mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti^+ and 2-fluoroethanol (FE) clusters seeded in 1.7 atm Ar. b_n : $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})(\text{FE})_n$; c_n : $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$; m_n : $(\text{FE})_n\text{H}^+$.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



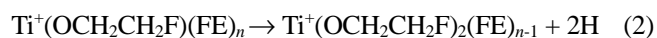
Scheme 1. Summary of the observed reaction pathways of $\text{Ti}^+ + \text{CH}_2\text{FCH}_2\text{OH}$ along with the calculated reaction energies (kcal/mol).

form $[\text{H}_2-\text{Ti}^+-\text{O}]$ because Ti^+ has three valence electrons.⁶ Alternatively, the $[\text{HO}-\text{Ti}^+-\text{CH}_2\text{CH}_2\text{F}]$ intermediate could produce TiFOH^+ followed by transfer of a F atom attached to the β -carbon and elimination of C_2H_4 . This pathway resembles reactions of $\text{Fe}^+ + \text{ClCH}_2\text{CH}_2\text{Br}$ and $\text{Co}^+ + \text{ClCH}_2\text{CH}_2\text{OH}$, in which the metal ion interacts with both functional groups in a five-membered ring configuration, leading to the formation of FeClBr^+ and CoClOH^+ , respectively, by elimination of ethylene.⁷ The calculation results also indicate that both the TiO^+ and TiFOH^+ product channels are thermodynamically favorable due to their high exothermicity (-107.8 and -148.5 kcal/mol, respectively).

As a major intracuster ion-molecule reaction channel, the Ti^+ ion can insert into the O-H bond of FE molecules within the parent $\text{Ti}^+(\text{FE})_m$ clusters, followed by H-elimination:



It is noteworthy that the $\text{Ti}^+\text{OCH}_2\text{CH}_2\text{F} + \text{H}$ formation channel is clearly observed within the heteroclusters even though it is slightly endothermic (7.4 kcal/mol). A surprising finding for $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$ ions is that H-elimination in FE by Ti^+ is possible for up to two FE molecules.



Within the stabilizing environs of a heterocluster, insertion of a $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})$ ion into a second FE molecule produces the $(\text{CH}_2\text{FCH}_2\text{O})\text{Ti}^+(\text{H})(\text{OCH}_2\text{CH}_2\text{F})$ intermediate. This intermediate then dissociates internally and $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2$ ion is produced *via* H-elimination. An abrupt decrease in the intensity of $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_m(\text{FE})_n$ cluster ions occurs for $m \geq 3$, which reflects the fact that the reactivity of the Ti^+ ion after $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_2(\text{FE})_n$ formation is strongly suppressed by the presence of the ethoxy ligands. This finding is supported by the results of a previous study of the intracuster reactions of Ti^+ with alcohol compounds containing different alkyl groups, which disclosed a large reduction in the reactivity of Ti^+ due to the steric hindrance of the alkyl radical.⁸

In conclusion, we have investigated ion-molecule reactions within mixed $\text{Ti}^+(\text{FE})_n$ heteroclusters using a combi-

nation of laser ablation and supersonic beam expansion. The observation of TiO^+ and TiFOH^+ ions is understood on the basis of a C-O insertion reaction followed by $\text{C}_2\text{H}_5\text{F}$ and C_2H_4 fragmentations, respectively. The intracuster ion-molecule reactions produce a major sequence of $\text{Ti}^+(\text{OCH}_2\text{CH}_2\text{F})_m(\text{FE})_n$ ions ($m = 1, 2$), which is attributed to sequential insertions of Ti^+ into the O-H bond of FE followed by H-eliminations. *Ab initio* calculations were carried out to study the reaction pathways and energetics of the proposed mechanisms.

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