Intracluster Ion-Molecule Reactions within Ti⁺(CH₂FCH₂OH)_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. The Ti⁻ ion activates C-C, C-H, and O-O bonds in specific gas-phase reactions. 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 Ti⁺(CH₂FCH₂OH)_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 bi-molecular ion-molecule collisions. The apparatus used in this work has been described previously. Briefly, laserablated species containing Ti⁺ ions traversed perpendicular to a supersonic beam of CH₂FCH₂OH clusters 1 cm away

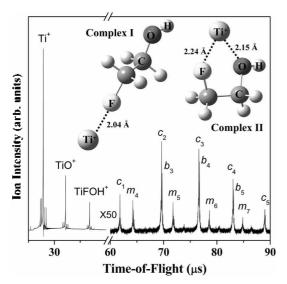


Figure 1. Mass spectrum of the cluster ions produced by reactive collisions of laser-ablated Ti⁻ and 2-fluoroethanol (FE) clusters seeded in 1.7 atm Ar. b_n . Ti⁺(OCH₂CH₂F)(FE)_n; c_n : Ti⁻(OCH₂CH₂-F)₂(FE)_n; m_n : (FE)_nH⁺. Ab initio calculations show the optimized ground-state structures for the two possible Ti⁻-FE complexes.

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 $(m \cdot e = 64)$ and TiFOH $(m \cdot e = 84)$ 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 Ti (OCH_2CH_2F) - $(FE)_n$ (denoted b_n), Ti (OCH_2CH_2F) - $(FE)_n$ (denoted c_n), and $(FE)_nH^+$ (denoted m_n). The presence of $(FE)_nH^-$ cluster ions can be attributed to intracluster protonation of the parent $(FE)_n^+$ 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. 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 fivemembered 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 $Ti^- + FE$, 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 [HO- Ti^- CH₂CH₂F] intermediate. This intermediate could undergo α -H atom transfer from the OH group to the Ti^+ ion, followed by CH₃CH₂F elimination, to produce TiO^+ . This mechanism is analogous to the $Ti^+ + H_2O \rightarrow TiO^- + H_2$ reaction, in which the dehydrogenation channel proceeds from a [H- Ti^- -OH] intermediate by a H migration from O to

$$Ti^{+} + CH_{2}FCH_{2}OH \longrightarrow F \xrightarrow{(i)} O - H$$

$$CH_{2} - CH_{2}$$

$$\xrightarrow{(i) C - O} [HO - Ti^{+} - CH_{2}CH_{2}] \xrightarrow{(a)} \{O - Ti^{+} - CH_{2}CH_{2}F\} \longrightarrow TiO^{+} + CH_{3}CH_{2}F (-107.8)$$

$$\xrightarrow{(b)} \left(HO - Ti^{+} - CH_{2}CH_{2}\right) \longrightarrow TiFOH^{+} + C_{2}H_{4} (-148.5)$$

$$\xrightarrow{(ii) O - H} [H - Ti^{+} - OCH_{2}CH_{2}F] \longrightarrow Ti^{+}OCH_{2}CH_{2}F + H (+7.4)$$

Scheme 1. Summary of the observed reaction pathways of Ti⁻ + CH₂FCH₂OH along with the calculated reaction energies (kcal/mol).

form [H₂-Ti⁺-O] because Ti⁻ has three valence electrons.⁶ Alternatively, the [HO-Ti⁻-CH₂CH₂F] intermediate could produce TiFOH⁺ followed by transfer of a F atom attached to the β-carbon and elimination of C₂H₄. This pathway resembles reactions of Fe⁺ + ClCH₂CH₂Br and Co⁻ + ClCH₂CH₂OH, 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 intracluster ion-molecule reaction channel, the Ti⁻ ion can insert into the O-H bond of FE molecules within the parent Ti⁻(FE)_m clusters, followed by H-elimination:

$$Ti^{+}(FE)_{m} \rightarrow [H-Ti^{+}-OCH_{2}CH_{2}F]^{+}(FE)_{m-1} \rightarrow Ti^{+}(OCH_{2}CH_{2}F)(FE)_{n} + H + (m-n-1)FE$$
 (1)

It is noteworthy that the Ti⁺OCH₂CH₂F + H formation channel is clearly observed within the heteroclusters even though it is slightly endothermic (7.4 kcal/mol). A surprising finding for Ti⁻(OCH₂CH₂F)₂(FE)_n ions is that H-elimination in FE by Ti⁺ is possible for up to two FE molecules.

$$Ti^{-}(OCH_{2}CH_{2}F)(FE)_{n} \rightarrow Ti^{+}(OCH_{2}CH_{2}F)_{2}(FE)_{n-1} + 2H$$
 (2)

Within the stabilizing environs of a heterocluster, insertion of a $Ti^+(OCH_2CH_2F)$ ion into a second FE molecule produces the $(CH_2FCH_2O)Ti^-(H)(OCH_2CH_2F)$ intermediate. This intermediate then dissociates internally and $Ti^-(OCH_2-CH_2F)_2$ ion is produced *via* H-elimination. An abrupt decrease in the intensity of $Ti^+(OCH_2-CH_2F)_m(FE)_n$ cluster ions occurs for $m \ge 3$, which reflects the fact that the reactivity of the Ti^+ ion after $Ti^-(OCH_2-CH_2F)_2(FE)_n$ formation is strongly suppressed by the presence of the ethoxy ligands. This finding is supported by the results of a previous study of the intracluster 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.

In conclusion, we have investigated ion-molecule reactions within mixed Ti⁻(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 C_2H_5F and C_2H_4 fragmentations, respectively. The intracluster ion-molecule reactions produce a major sequence of $Ti^+(OCH_2CH_2F)_{mi}$ (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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