

Communications

Competitive Ion-Molecule Reactions within $V^+(\text{CH}_3\text{COOCH}_3)_n$ Clusters

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The importance of transition metal ions in catalyzing the chemical reactions of various organic molecules has prompted extensive experimental and theoretical studies aimed at understanding the catalytic activity of such ions. In this context, the examination of gas phase ion-molecule reactions within heteroclusters, which avoids the complications arising from solvent environments and crystalline forces, has great potential for the detailed elucidation of the catalytic activities of transition metal ions and of the changes in the reaction pathways as a function of cluster size.¹

In the present study, we investigated gas phase $V^+(\text{CH}_3\text{COOCH}_3)_n$ heterocluster systems to unravel the competitive ion-molecule reactions within the ionized clusters and to elucidate reactive pathways not ordinarily found in bimolecular ion-molecule collisions. The experimental apparatus used in this work has been described elsewhere.² In brief, laser ablated species containing V^+ ions traversed perpendicular to a supersonic beam of methyl acetate (MeAc, $\text{CH}_3\text{COOCH}_3$) clusters 1 cm away from a rotating target, where they reacted with the reactant clusters. The product ions were then analyzed using a reflectron

time-of-flight mass spectrometer. Figure 1 shows a typical time-of-flight (TOF) mass spectrum obtained when V^+ reacts with MeAc. The reaction products can be divided into two groups: (i) V^+ -containing clusters (a_n , b_n , c_n , d_n series) and (ii) VO^+ -containing clusters (e_n , f_n , t_n series). The formation of these cluster ions implies that V^+ readily reacts with MeAc molecules solvated within intact $V^+(\text{MeAc})_n$ (denoted a_n) heteroclusters. The dominant t_n and e_n series ions in the high mass region reveal the effective oxidation reaction of the V^+ ion.

To interpret the formation mechanism of VO^+ ion via an oxidation pathway, we calculated potential energy surfaces for two plausible reactions: (1) V^+ insertion into the C=O bond from Complex I (Figure 2a); (2) V^+ insertion into the C-O bond from Complex II (Figure 2b). Complex I represents the case in which the V^+ ion approaches the O atom of the carbonyl group, thereby activating the C=O bond. Complex II corresponds to the case in which the V^+ ion interacts with the O atom of the methoxy group, which is a feasible route for C-O bond insertion. The molecular geometries (reactant, product, intermediates, and transition states) of both triplet and quintet states were fully optimized at B3LYP/6-311++G(d,p) level using the Gaussian 03W package.^{3,4} The geometries of the stationary points are depicted in the Supporting Information, where the superscript denotes the spin multiplicity. IM and TS represent the intermediate and the transition state, respectively.

Once the association Complex I (${}^2\text{IM}_1$) is formed (Figure 2a), V^+ insertion into the C=O bond produces the complex ${}^3\text{IM}_2$ via intersystem crossing. This intermediate could undergo α -H atom transfer from the CH_3 group to the β -C atom (${}^3\text{IM}_3 \rightarrow {}^3\text{IM}_4$), followed by $\text{CH}_2=\text{CHOCH}_3$ elimination, to produce the VO^+ ion. On the other hand, the C-O bond insertion by V^+ ion can convert Complex II (${}^2\text{IM}_5$ in Figure 2b) into the three-membered complex ${}^3\text{IM}_6$. Intramolecular CH_3 migration to the central carbon atom of the ${}^3\text{IM}_6$ via transition state ${}^3\text{TS}_{67}$ yielded the ${}^3\text{IM}_7$ which can be considered as a product complex. Considering the reaction energies, the C=O insertion channel is likely to be the favorable oxidation pathway of V^+ ion because it has lower activation energy than C-O insertion channel.

Figure 2c provides a summary of the reaction pathways of $V^+ + \text{MeAc}$, along with the calculated reaction energies. Zero-

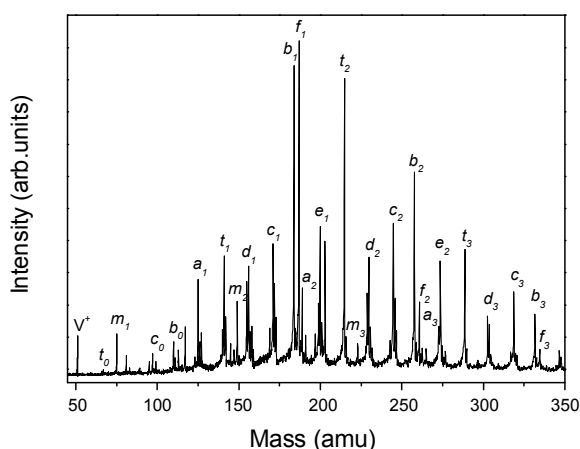


Figure 1. Mass spectrum of heterocluster ions formed by laser-ablated V^+ and methyl acetate (MeAc) clusters. a_n : $V^+(\text{MeAc})_n$; b_n : $V^+(\text{CH}_3\text{COO})(\text{MeAc})_n$; c_n : $V^+(\text{CH}_3\text{OCH}_3)(\text{MeAc})_n$; d_n : $V^+(\text{OCH}_3)(\text{MeAc})_n$; e_n : $\text{VO}^+(\text{CH}_3\text{COO})(\text{MeAc})_n$; f_n : $\text{VO}^+(\text{CH}_3\text{OCH}_3)(\text{MeAc})_n$; t_n : $\text{VO}^+(\text{MeAc})_n$; m_n : $(\text{MeAc})_n\text{H}^+$.

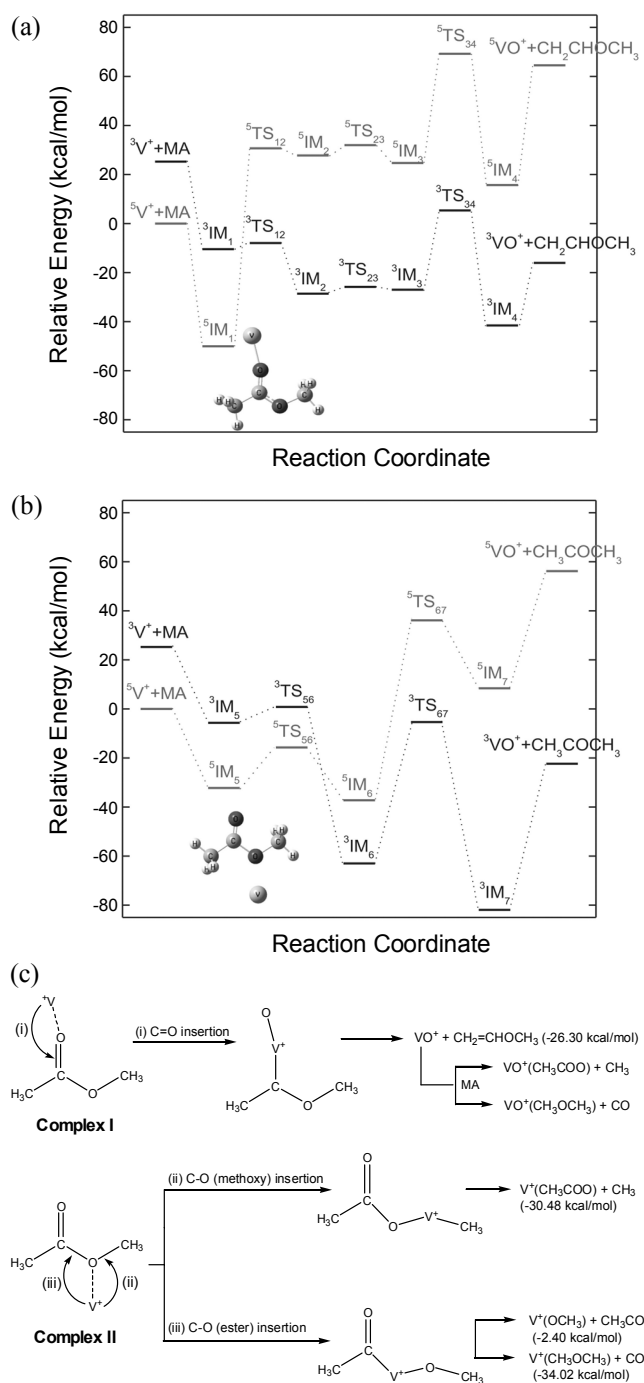


Figure 2. (a) Potential energy surfaces of the V^+ insertion into the C=O bond of MeAc. (b) Potential energy surfaces of the V^+ insertion into the C-O bond. (c) Summary of the observed reaction channels of $V^+ + MeAc$ along with the calculated reaction energies (kcal/mol).

point-energy corrections were included when calculating the reaction energies. The reaction pathways can be divided into three categories: (i) C=O bond activation, (ii) C-O bond (methoxy) activation, and (iii) C-O bond (ester) activation. As mentioned above, V^+ is most efficiently oxidized by MeAc through the reaction of Complex I. Within the stabilizing environs of a heterocluster, the insertion of a VO^+ ion into a second MeAc molecule produces $VO^+(CH_3COO)(MeAc)_n$ (e_n series) or $VO^+(CH_3OCH_3)(MeAc)_n$ (f_n series) heteroclusters via similar re-

action pathways, denoted (ii) and (iii) in Figure 2c, respectively.

As a competing pathway by which V^+ can react with MeAc, the V^+ ion can insert into the C-O bond of the methoxy group within Complex II followed by CH_3 -elimination to produce $V^+(CH_3COO) + CH_3$. The exothermicity of this reaction, -30.48 kcal/mol, suggests that this reaction will occur. Complex II can also react with V^+ to form the $[H_3CCO-V^+-OCH_3]$ intermediate by V^+ insertion into the C-O bond of the ester group; hence a $V^+(OCH_3)$ ion is expected to form via V^+-C bond rupture. Alternatively, the $[H_3CCO-V^+-OCH_3]$ intermediate could produce $V^+(CH_3OCH_3)$ followed by transfer of a CH_3 group attached to the carbonyl group and elimination of CO. This is consistent with a view that activation of methane by transition metal oxides undergoes a CH_3 migration to form a molecular complex between the metal atom and the methanol.⁵ The calculation results also indicate that both the $V^+(OCH_3)$ and $V^+(CH_3OCH_3)$ product channels are exothermic (-2.40 and -34.02 kcal/mol, respectively) and hence thermodynamically favorable. The potential energy surface diagrams associated with the V^+ insertion reactions (pathway (ii) and (iii) in Figure 2c) will be described in a forthcoming paper.

In conclusion, we have investigated the competitive insertion reactions of V^+ within $V^+(MeAc)_n$ heteroclusters using a combination of laser ablation and supersonic beam expansion. The mass spectrum exhibited peaks corresponding to two types of reaction products: (a) V^+ -containing clusters (a_n, b_n, c_n, d_n series) and (b) VO^+ -containing clusters (e_n, f_n, t_n series). The $V^+(OCH_3)(MeAc)_n$ and $V^+(CH_3COO)(MeAc)_n$ ions are attributed to the insertion of a V^+ ion into the C-O bond of MeAc. The observation of the $VO^+(MeAc)_n$ ion series is understood on the basis of a C=O insertion reaction followed by H atom transfer and CH_2CHOCH_3 elimination. In addition, sequential reactions of VO^+ ions are also observed. Density functional theory calculations were performed to rationalize the reaction pathways and energetics of the proposed mechanism.

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Supporting Information. The Supporting Information is available on request from the correspondence author (E-mail: kwjung@wku.ac.kr).

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