Reactions of Group V Transition Metal Oxide Cluster Ions with Ethane and Ethylene

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Reactions of mass-selected group V transition metal oxide cluster ions ($V_xO_y^{\pm}$, $Nb_xO_y^{\pm}$, and $Ta_xO_y^{\pm}$) with ethane (C_2H_6) and ethylene (C_2H_4) were investigated. The major reaction channels observed during the reactions of C_2 hydrocarbons with $M_xO_y^+$ were association and oxygen transfer. The association channel, $M_xO_yC_2H_n^+$, where $n = 4$ or 6, was common to most of the group V transition metal oxide cluster cations examined. However, a reaction channel corresponding to the loss of an oxygen atom from the mass-selected metal oxide cluster, producing $M_xO_{y-1}^+$, was only observed during the reactions of $(V_2O_5)_n^+$, where $n = 1$, 2, or 3, with ethane and ethylene and during the reactions of ethylene with $Nb_2O_5^+$. It is proposed that this reaction pathway is oxygen transfer from the mass-selected metal oxide cluster cation to the neutral hydrocarbon. This oxygen transfer channel is the major pathway observed during the course of reactions of $V_2O_5^+$, $V_4O_{10}^+$, and $V_6O_{15}^+$ with ethane and ethylene, but this reaction pathway is minor or nonexistent in the case of reactions of C_2H_6 and C_2H_4 with stoichiometrically equivalent niobium and tantalum oxide cluster cations. Additionally, the reactions of $M_xO_y^-$ with C_2 hydrocarbons were also examined. In contrast to the cation results, no reaction products were observed in studies of the interaction of group V transition metal oxide cluster anions with ethane and ethylene. The studies reveal that the identity of the metal, charge state, cluster stoichiometry, and geometric structure strongly influence the ability of the metal oxide cluster to transfer an oxygen atom to the neutral C_2 hydrocarbon.

Introduction

There is considerable interest in the selective oxidation of hydrocarbons over transition metal oxide catalysts because these reactions are the basis of numerous industrial processes yielding organic oxides, such as aldehydes and organic acids.[1] The key to understanding the selectivity and activity of catalysts lies in the unambiguous identification of both the reaction mechanisms and the active sites present on a catalytic surface. However, the nature of the catalytically active sites and the mechanism of selective oxidation are still in question, which impedes the development of effective hydrocarbon oxidation catalysts.[2] Consequently, knowledge of the fundamental mechanistic steps, characterization of the reaction intermediates, and the elucidation of structure−reactivity relationships is of unprecedented importance in providing fundamental information that is necessary to develop more efficient and selective oxidation catalysts.

Catalytic materials have been extensively examined to understand the mechanisms by which processes, such as oxygen transfer, occur on condensed phase surfaces. However, it is difficult to fully interpret the results due to the multitude of defects found on surfaces and the complexity associated with such large systems. An alternate way to describe a complex metal oxide surface is as a collection of clusters of different sizes and isomers.[3] Consequently, gas-phase clusters provide an ideal, controlled environment to explore various types of reactive sites that may influence catalytic activity on metal oxide surfaces.[4] The examination of reactions of gas phase metal oxide clusters of differing composition, stoichiometry, size, oxidation state, degree of coordinative saturation, and charge state with organic molecules offers the prospect of gaining considerable new insights into the basis of catalytic activity on metal oxide surfaces. The reaction products obtained in gas phase studies render valuable information about reaction intermediates and mechanisms and consequently allow for an excellent opportunity to study fundamental oxygen transfer reactions.

This paper is a continuation of work in our laboratory on the reactivity of group V transition metal oxide cluster ions with hydrocarbons.[5−8] The results reported herein are of reactions of group V transition metal oxide cluster ions with ethane and ethylene. Early transition metal oxide catalysts are under scrutiny because of their importance in catalytic reactions. For example, vanadium oxides are key catalysts in the selective oxidation and ammoxidation of hydrocarbons.[9,10] Recently, there has been an interest in the catalytic properties of other group V transition metal oxides. For example, niobium oxide surfaces have been found to exhibit extraordinary catalytic properties in selective oxidation reactions and hydrocarbon conversions.[11] Finally, condensed phase studies on tantalum oxides have revealed some intriguing catalytic properties, such as the ability to efficiently catalyze the vapor phase Beckmann rearrangement and the vapor phase decomposition of methyl *tert*-butyl ether.[12,13] The current investigation was performed in order to examine the effect that different transition metals in the same group of the periodic table have on the oxygen transfer reaction from mass-selected group V transition metal oxide clusters to the neutral C_2 hydrocarbon. Additionally, new fundamental insights gained from these gas-phase studies can provide information for the molecular engineering of more effective oxidation catalysts.

Experimental Section

A guided ion beam mass spectrometer coupled with a laser vaporization source, which has been described in detail previ-

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TABLE 1: Reactions of Group V Transition Metal Oxide Cluster Cations with 0.15 MTorr of Ethane

cluster	$V_xO_y^+$ reaction products	$Nb_xO_y^+$ reaction products	$Ta_xO_y^+$ reaction products
$M_2O_4^+$	$V_2O_4C_2H_6^+$	$Nb_2O_4C_2H_6^+$	$Ta_2O_4C_2H_6^+$
$M_2O_5^+$	$V_2O_4^+$ $V_2O_5C_2H_6^+$	$Nb_2O_5C_2H_6^+$	$Ta_2O_5C_2H_6^+$
$M_2O_6^+$	$V_2O_4^+$ $V_2O_6C_2H_6^+$	$Nb_2O_4^+$ $Nb_2O_6C_2H_6^+$	$Ta_2O_4^+$ $Ta_2O_6C_2H_6^+$
$M_3O_6^+$	$V_3O_6C_2H_6^+$		
$M_3O_7^+$	$V_3O_7C_2H_6^+$	$Nb_3O_7C_2H_6^+$	$Ta_3O_7C_2H_6^+$
$M_3O_8^+$	$V_3O_6^+$ $V_3O_8C_2H_6^+$	$Nb_3O_8C_2H_6^+$	$Ta_3O_8C_2H_6^+$
$M_3O_9^+$	- -	$Nb_3O_7^+$ $Nb_3O_9C_2H_6^+$	$Ta_3O_7^+$ $Ta_3O_9C_2H_6^+$
$M_4O_9^+$	NR	NR	NR
$M_4O_{10}^+$	$V_4O_9^+$	NR	NR
$M_4O_{11}^+$	$V_4O_9^+$ $V_4O_{11}C_2H_6^+$	NR	NR
$M_4O_{12}^+$	- -	$Nb_4O_{10}^+$	$Ta_4O_{10}^+$
$M_5O_{12}^+$	$V_5O_{12}C_2H_6^+$	$Nb_5O_{12}C_2H_6^+$	$Ta_5O_{12}C_2H_6^+$
$M_5O_{13}^+$	$V_5O_{13}C_2H_6^+$	$Nb_5O_{13}C_2H_6^+$	$Ta_5O_{13}C_2H_6^+$
$M_6O_{14}^+$	NR		
$M_6O_{15}^+$	$V_6O_{14}^+$		

ously,[14] is used to examine the reactions of mass-selected group V transition metal oxide cluster ions with ethane and ethylene. The second harmonic output of a Nd:YAG laser (5−20 mJ/pulse, 20 Hz) is focused onto the metal rod, which is translated and rotated so that each pulse of the laser beam ablates a fresh metal surface. A pulsed valve is used to introduce a mixture of oxygen seeded in helium (ca. 8%) over the ablated metal surface, where plasma reactions occur and group V transition metal oxide clusters are produced. The clusters exit the source, where they are further cooled by supersonic expansion; thereafter they pass through a 3 mm skimmer to the first set of electrostatic lenses, which is used to guide and focus the ion beam. The clusters enter the first quadrupole, which allows the ion of interest, $M_xO_y^{\pm}$, to be mass-selected from the cluster distribution. The mass-selected cluster proceeds through a second set of electrostatic lenses into an octopole ion guide, where reactions with ethane or ethylene occur. A capacitance manometer (MKS) is used to monitor the pressure of the gas in the octopole. After the reactions occur in the octopole, the product ions exit and are guided by a third set of electrostatic lenses into the second quadrupole, where the products are mass analyzed. Detection of the products is achieved using a dynode channel electron multiplier. The signal goes through a preamplifier−discriminator and is stored with a personal computer via a multichannel scalar card.

Results

The reactions of group V transition metal oxide cluster ions ($M_xO_y^{\pm}$) with C_2 hydrocarbons have been investigated in our laboratory. The reaction pathways observed during reactions of $M_xO_y^+$ with ethane and ethylene under thermal energy conditions include association of the hydrocarbon, $M_xO_yC_2H_6^+$ or $M_xO_yC_2H_4^+$, and atomic oxygen loss, $M_xO_{y-1}^+$, from the mass-selected metal oxide cluster. Tables 1 and 2 summarize the reaction products of group V transition metal oxide cluster cations with 0.15 mTorr of ethane and ethylene at thermal energies. Single collision conditions are observed under 0.10 mTorr of reactant gas in the octopole. In addition, the reactions of M_xO_y anions with ethane and ethylene have been explored in order to determine the effect of charge state on these reactions. Interestingly, the reactions of $M_xO_y^-$ with ethane and ethylene generated no observable reaction products.

TABLE 2: Reactions of Group V Transition Metal Oxide Cluster Cations with 0.15 MTorr of Ethylene

cluster	$V_xO_y^+$ reaction products	$Nb_xO_y^+$ reaction products	$Ta_xO_y^+$ reaction products
$M_2O_4^+$	$V_2O_4C_2H_4^+$	$Nb_2O_4C_2H_4^+$	$Ta_2O_4C_2H_4^+$
$M_2O_5^+$	$V_2O_3^+$ $V_2O_4^+$ $V_2O_5C_2H_4^+$	$Nb_2O_4^+$ $Nb_2O_5C_2H_4^+$	$Ta_2O_5C_2H_4^+$
$M_2O_6^+$	$V_2O_4^+$ $V_2O_4C_2H_4^+$ $V_2O_6C_2H_4^+$	$Nb_2O_4^+$ $Nb_2O_6C_2H_4^+$	$Ta_2O_4^+$ $Ta_2O_6C_2H_4^+$
$M_3O_6^+$	$V_3O_6C_2H_4^+$		
$M_3O_7^+$	$V_3O_7C_2H_4^+$	$Nb_3O_7C_2H_4^+$	$Ta_3O_7C_2H_4^+$
$M_3O_8^+$	$V_3O_6^+$ $V_3O_6C_2H_4^+$	$Nb_3O_8C_2H_4^+$	$Ta_3O_8C_2H_4^+$
$M_3O_9^+$	- -	$Nb_3O_7^+$	$Ta_3O_7^+$ $Ta_3O_9C_2H_4^+$
$M_4O_9^+$	$V_4O_9C_2H_4^+$	NR	NR
$M_4O_{10}^+$	$V_4O_8^+$ $V_4O_9^+$ $V_4O_9C_2H_4^+$	$Nb_4O_{10}C_2H_4^+$	$Ta_4O_{10}C_2H_4^+$
$M_4O_{11}^+$	$V_4O_9^+$ $V_4O_9C_2H_4^+$	$Nb_4O_9^+$ $Nb_4O_{11}C_2H_4^+$	$Ta_4O_9^+$ $Ta_4O_{11}C_2H_4^+$
$M_4O_{12}^+$	- -	$Nb_4O_{10}^+$	$Ta_4O_{10}^+$
$M_5O_{12}^+$	$V_5O_{12}C_2H_4^+$	$Nb_5O_{12}C_2H_4^+$	$Ta_5O_{12}C_2H_4^+$
$M_5O_{13}^+$	$V_5O_{13}C_2H_4^+$	$Nb_5O_{13}C_2H_4^+$	$Ta_5O_{13}C_2H_4^+$
$M_6O_{14}^+$	$V_6O_{14}C_2H_4^+$		
$M_6O_{15}^+$	$V_6O_{13}^+$ $V_6O_{14}^+$		

(1) Reactions of Vanadium Oxide Cluster Cations ($V_xO_y^+$) with Ethane and Ethylene. Reactions of mass-selected vanadium oxide cluster cations ($V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{9-11}^+$, $V_5O_{12,13}^+$, and $V_6O_{14,15}^+$) with C_2 hydrocarbons have been examined. The major products in the reactions of $V_xO_y^+$ with ethane and ethylene are association of the hydrocarbon and atomic oxygen loss. Most of the stoichiometric vanadium oxide cluster cations, except $V_4O_9^+$ and $V_6O_{14}^+$ displayed an association channel, $V_xO_yC_2H_6^+$, during reactions with ethane. Furthermore, all of the stoichiometric vanadium oxide cluster cations exhibited an association channel, $V_xO_yC_2H_4^+$, during reactions with ethylene. Particular oxygen-rich clusters, $V_2O_5^+$, $V_4O_{10}^+$, and $V_6O_{15}^+$, displayed an atomic oxygen loss channel during reactions with ethane and ethylene, which occurred via reaction 1, where $n = 4$ or 6

$$V_xO_y^+ + C_2H_n \rightarrow V_xO_{y-1}^+ + (C_2H_nO) \tag{1}$$

Our experimental apparatus cannot determine the identity of neutral species formed during these reactions and we do not mean to specifically identify the neutral product in parentheses. It is only our intention to illustrate that a single oxygen atom is most likely transferred from the mass-selected vanadium oxide cluster to the C_2 hydrocarbon. The conclusion that reaction 1 is an oxygen transfer reaction from the mass-selected cluster to ethane or ethylene is supported by the observation that $V_2O_5^+$, $V_4O_{10}^+$, and $V_6O_{15}^+$ do not lose a single oxygen atom during collision-induced dissociation studies at near thermal energy under single collision conditions.[5] The reactivities of the remaining oxygen-rich clusters, $V_2O_6^+$, $V_3O_8^+$, and $V_4O_{11}^+$, with ethane and ethylene were also probed and one of the major reaction channels observed is loss of molecular oxygen, which is shown in reaction 2

$$V_xO_y^+ + C_2H_n \rightarrow V_xO_{y-2}^+ + O_2 + C_2H_n \tag{2}$$

Additionally, $V_2O_6^+$, $V_3O_8^+$, and $V_4O_{11}^+$ displayed a replacement reaction channel during reactions with ethylene as depicted

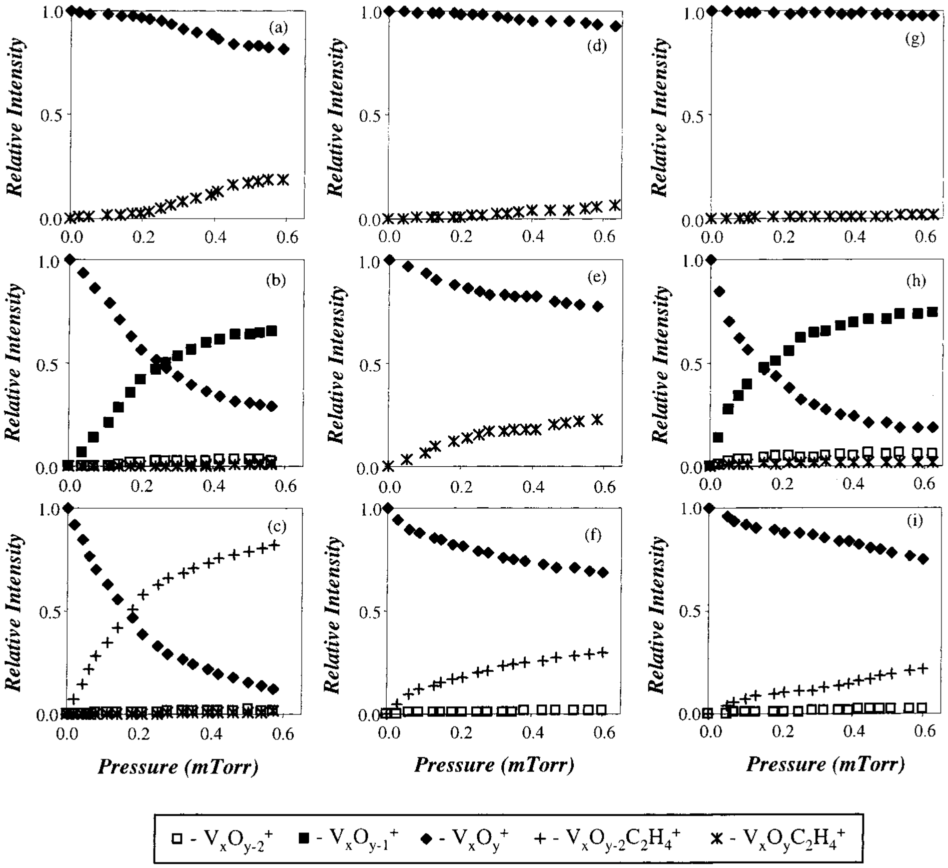

Figure 1. Branching ratios of (a, b, c) $V_2O_{4-6}^+$, (d, e, f) $V_3O_{6-8}^+$, and (g, h, i) $V_4O_{9-11}^+$ with ethylene. Note how atomic oxygen loss, $V_xO_{y-1}^+$, is the major product formed in the reactions of $V_2O_5^+$ and $V_4O_{10}^+$ with ethylene.

by reaction 3

$$V_xO_y^+ + C_2H_4 \rightarrow V_xO_{y-2}C_2H_4^+ + O_2 \qquad (3)$$

This replacement reaction probably does occur during the reactions of $V_2O_6^+$, $V_3O_8^+$, and $V_4O_{11}^+$ with ethane, but the mass of the $V_xO_{y-2}C_2H_6^+$ product is only two amu less than the selected peak. The resolution of the second quadrupole was increased in order to separate these two peaks; however, by increasing the resolution, the selected ion intensity was greatly diminished and the presence of the $V_xO_{y-2}C_2H_6^+$ product could not be confirmed or denied.

(2) Reactions of Niobium Oxide Cluster Cations ($Nb_xO_y^+$) with Ethane and Ethylene. Reactions of mass-selected niobium oxide cluster cations ($Nb_2O_{4-6}^+$, $Nb_3O_{7-9}^+$, $Nb_4O_{9-12}^+$, and $Nb_5O_{12,13}^+$) with ethane and ethylene revealed that association and oxygen transfer are the only reaction pathways observed. An association channel, $Nb_xO_yC_2H_n^+$, was observed for the reactions of most of the niobium oxide cluster cations, except $Nb_4O_9^+$ and $Nb_4O_{12}^+$, with C_2 hydrocarbons. $Nb_2O_5^+$ displayed an oxygen transfer reaction channel during reactions with ethylene, according to reaction 4

$$Nb_2O_5^+ + C_2H_4 \rightarrow Nb_2O_4^+ + (C_2H_4O) \qquad (4)$$

As in the case of vanadium oxide clusters, it is proposed that reaction 4 is an oxygen transfer reaction from the cluster to the neutral hydrocarbon because $Nb_2O_5^+$ does not lose a single oxygen atom during collision-induced dissociation studies at near thermal energy under single collision conditions.[8] Additionally, reactions of the oxygen-rich niobium oxide cluster cations, $Nb_2O_6^+$, $Nb_3O_9^+$, and $Nb_4O_{11,12}^+$, with C_2 hydrocarbons were also investigated. These oxygen-rich clusters exhibited loss of molecular oxygen during reactions with ethane and ethylene. The same reaction pathway, which is shown in reaction 2, was also observed during reactions of oxygen-rich niobium oxide cluster cations with C_2 hydrocarbons.

(3) Reactions of Tantalum Oxide Cluster Cations ($Ta_xO_y^+$) with Ethane and Ethylene. Reactions of mass-selected tantalum oxide cluster cations ($Ta_2O_{4-6}^+$, $Ta_3O_{7-9}^+$, $Ta_4O_{9-12}^+$, and $Ta_5O_{12,13}^+$) with ethane and ethylene also were examined. The reaction pathways observed include hydrocarbon association and molecular oxygen loss. Most of the tantalum oxide cluster cations displayed an association channel, $Ta_xO_yC_2H_n^+$, during reactions with C_2 hydrocarbons. As opposed to vanadium and niobium oxide systems, atomic oxygen loss was not observed during the reactions of any of the tantalum oxide cluster cations with ethane or ethylene. Additionally, the reactions of oxygen-rich tantalum oxide cluster cations, $Ta_2O_6^+$, $Ta_3O_9^+$, and $Ta_4O_{11,12}^+$, with C_2 hydrocarbons were investigated. Molecular oxygen loss in accord with reaction 2 was the major reaction product observed during reactions of oxygen-rich tantalum oxide clusters with ethane and ethylene.

Discussion

Figures 1 and 2 display the branching ratios of $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, and $V_4O_{9-11}^+$ with ethylene and ethane, respectively. Most of the vanadium oxide clusters shown in Figures 1 and 2 exhibit relatively minor reaction products, such as association of ethane or ethylene and loss of molecular oxygen. However, the most notable characteristic of Figures 1 and 2 is the significant atomic oxygen loss channel, $V_xO_{y-1}^+$, that is observed during the reactions of $V_2O_5^+$ and $V_4O_{10}^+$ with ethane

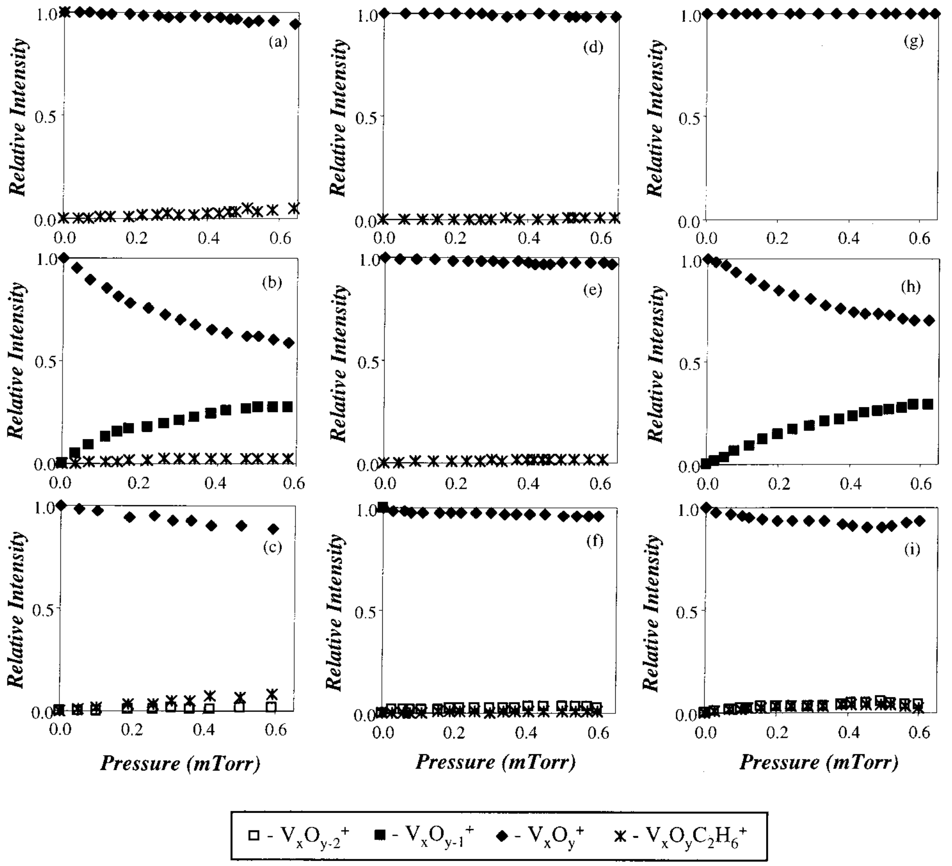

Figure 2. Branching ratios of (a, b, c) $V_2O_{4-6}^+$, (d, e, f) $V_3O_{6-8}^+$, and (g, h, i) $V_4O_{9-11}^+$ with ethane. Note how atomic oxygen loss, $V_xO_{y-1}^+$, is the major product formed in the reactions of $V_2O_5^+$ and $V_4O_{10}^+$ with ethane.

and ethylene. It should be mentioned that $V_6O_{15}^+$ also displayed a significant atomic oxygen loss channel, similar to Figures 1(b), 1(h), 2(b), and 2(h), during reactions with ethane and ethylene. This reaction pathway is not observed during the reactions of ethane or ethylene with any of the other vanadium oxide clusters examined, which is evident from Figures 1 and 2 and Tables 1 and 2. Therefore, it can be concluded that only vanadium oxide clusters with the stoichiometry $(V_2O_5)_n^+$, where $n = 1, 2,$ or 3, have the ability to exhibit an atomic oxygen loss channel during reactions with ethane and ethylene. To determine the effect of the cluster composition on reactivity, the reactions of niobium and tantalum oxide cluster cations with ethane and ethylene have also been investigated in this study. Figure 3 shows the branching ratios of $Nb_2O_5^+$ and $Ta_2O_5^+$ with ethylene. This figure demonstrates that a minor atomic oxygen loss channel is observed during the reaction of $Nb_2O_5^+$ with ethylene, whereas no atomic oxygen loss is observed during the reaction of $Ta_2O_5^+$ with ethylene. Furthermore, Figure 4 indicates that both $Nb_4O_{10}^+$ and $Ta_4O_{10}^+$ only exhibit association of ethane and do not display atomic oxygen loss during reactions with C_2H_6. Upon examination of Tables 1 and 2, it is apparent that atomic oxygen loss is only observed during the reactions of ethane with $(V_2O_5)_n^+$ and of ethylene with $(V_2O_5)_n^+$ and $Nb_2O_5^+$. Additionally, it is evident upon comparison of the branching ratios of $(M_2O_5)_n^+$ with ethane and ethylene in Figures 1 through 4 that the ability of $(V_2O_5)_n^+$ to exhibit atomic oxygen loss during reactions with ethane and ethylene is much greater than that of $(Nb_2O_5)_n^+$ or $(Ta_2O_5)_n^+$.

In the mass spectrometry experiments reported herein, the nature of the neutral species formed during reactions of $M_xO_y^+$ with C_2 hydrocarbons cannot be directly determined. However, it is believed that a single oxygen atom is transferred from the mass-selected group V transition metal oxide cluster to the C_2 hydrocarbon, as shown in reactions 1 and 4. All of the collision-induced dissociation results that are mentioned throughout this paper (unless otherwise mentioned) are at single collision conditions, which corresponds to less than 0.10 mTorr of gas in the octopole. Prior collision-induced dissociation results of $(M_2O_5)_n^+$ using xenon as the target gas demonstrate that these clusters do not exhibit an atomic oxygen loss channel at near thermal energy.[5,8,15] Furthermore, the collision-induced dissociation of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ with 0.08 mTorr Xe does

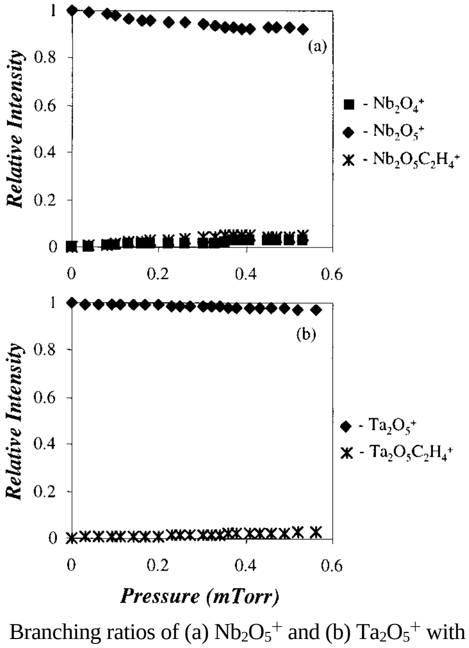

Figure 3. Branching ratios of (a) $Nb_2O_5^+$ and (b) $Ta_2O_5^+$ with ethylene.

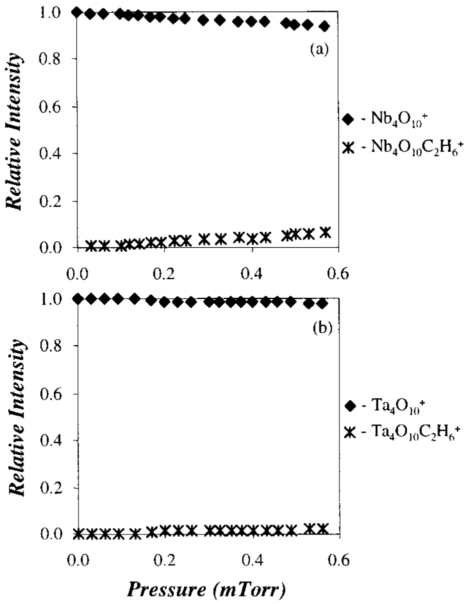

Figure 4. Branching ratios of (a) $Nb_4O_{10}^+$ and (b) $Ta_4O_{10}^+$ with ethane.

not result in loss of atomic or molecular oxygen at near thermal energy or a center-of-mass energy in excess of 3 eV.[15] Collision-induced dissociation of $(V_2O_5)_n^+$, where $n = 2$ or 3, has revealed that molecular oxygen is lost from these clusters upon collision with an inert gas at near thermal energy, which indicates that these clusters have oxygen-rich character.[5] The loss of a single oxygen atom from $V_4O_{10}^+$ or $V_6O_{15}^+$ is not observed during collision-induced dissociation experiments at near thermal energy or at a center-of-mass energy in excess of 3 eV. However, atomic oxygen loss is observed when $V_2O_5^+$ collides with 0.08 mTorr of Kr at $E_{CM} \geq 1.0$ eV, but loss of a single oxygen atom at this pressure is not observed at near thermal energy.[5] Molecular oxygen loss is also observed during CID experiments on $V_2O_5^+$ at $E_{CM} \geq 2$ eV. During reactions of $(M_2O_5)_n^+$ with ethane and ethylene, there is no collision energy added to the octopole rods under the conditions where the loss of a single oxygen atom occurs. Additionally, it should be noted that reaction 1 does occur at single collision conditions, which is apparent in Figures 1(b), 1(h), 2(b), and 2(h) because the $V_xO_{y-1}^+$ reaction channel is observed below 0.10 mTorr of C_2 hydrocarbon gas in the octopole. On the basis of the above evidence that loss of atomic oxygen loss is not observed upon collision of an inert gas with $(M_2O_5)_n^+$ at near thermal energy under single collision conditions, it is believed that the atomic oxygen loss channel, $M_xO_{y-1}^+$, observed during reactions of $(V_2O_5)_n^+$ with ethane and ethylene and $Nb_2O_5^+$ with ethylene is the result of an oxygen atom being transferred from $(M_2O_5)_n^+$ to the C_2 hydrocarbon, as shown in reactions 1 and 4.

It is evident from Figures 1 through 4 that the reactivity and product distribution of group V transition metal oxide cations, $M_xO_y^+$, with ethane and ethylene are significantly affected by the nature of the metal. Figures 1 and 2 show that oxygen transfer to the neutral hydrocarbon is the major product that is observed during reactions of $(V_2O_5)_n^+$ with ethane and ethylene. However, Figures 3 and 4 show that the oxygen transfer reaction pathway is either very minor or nonexistent during reactions of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ with ethane and ethylene. As discussed in a previous publication on the reactions of niobium and tantalum oxide cluster ions with *n*-butane, it is possible that the unique ability of vanadium oxide cluster cations to transfer an oxygen atom to a hydrocarbon compared to niobium and tantalum oxide cluster cations may be due in part to the availability of various stable oxidation states and the metal−oxygen bond energy.[7] The transfer of an oxygen atom from the metal oxide cluster to the organic substrate would cause a change in the oxidation state of a metal. The chemistry of vanadium, niobium, and tantalum is dominated by complexes that possess metal atoms in the (+5) oxidation state.[16] Vanadium atoms also exist in different formal oxidation states that vary from two to five, whereas niobium is only stable in the (+3) and (+5) oxidation state and the only stable oxidation state of tantalum is (+5). Therefore, it is possible that the ability of vanadium atoms to possess multiple stable oxidation states, unlike niobium and tantalum, is an important characteristic which facilitates the transfer of an oxygen atom from $(V_2O_5)_n^+$ to ethane or ethylene. Additionally, in order for oxygen transfer from $(M_2O_5)_n^+$ to a C_2 hydrocarbon to occur, at least one metal−oxygen bond of the cluster must be broken. The trend of the $M^+{-}O$ bond dissociation energy values, where M is a group V transition metal, as reported in the literature indicate that $V^+{-}O$ is the weakest bond, whereas the $Ta^+{-}O$ is the strongest bond.[17] It is recognized that the bond strength changes depending on the number of metal and oxygen atoms present in a cluster. However, the same general trend is expected with metal−oxygen bonds being the weakest in vanadium oxide clusters and strongest in tantalum oxide clusters. Because the metal−oxygen bonds present in vanadium oxide cluster cations are weaker than the stoichiometrically equivalent $M^+{-}O$ bonds of niobium and tantalum oxide cluster cations, it is possible that the main reaction pathway observed during reactions of $V_xO_y^+$ with ethane and ethylene is oxygen transfer. Furthermore, the oxygen transfer pathway might not be observed during reactions of niobium and tantalum oxide cluster cations with ethane and ethylene because the strong metal−oxygen bonds present in these clusters might not allow transfer of an oxide ligand to the neutral substrate. Although it is probable that the unique ability of $(V_2O_5)_n^+$ to transfer an oxygen atom to C_2 hydrocarbons compared to $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ can be attributed to the availability of several stable oxidation states to vanadium and the weaker vanadium−oxygen bond strength, it is thought that the geometric structure of $(V_2O_5)_n^+$ clusters also plays a vital role in their ability to transfer an oxygen atom to C_2 hydrocarbons. Likewise, it is also thought that the geometric structure of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ might play a crucial part in their inability to easily transfer an oxygen atom to ethane or ethylene.

The complex reactivity pattern as a function of cluster stoichiometry shown in Figures 1 and 2 and the similar behavior observed during the reactions of $V_6O_{15}^+$ with ethane and ethylene suggests that the $(V_2O_5)_n^+$ clusters, where $n = 1$, 2, or 3, contain a reactive center toward oxygen transfer, whereas the other vanadium oxide clusters examined do not. On the basis of these results, it is concluded that cluster stoichiometry is a key factor in the reactivity that is observed. It is thought that the vanadium oxide cluster cations with the stoichiometry $(V_2O_5)_n^+$ might possess similar structural features, which enables these particular clusters to readily transfer an oxygen atom to ethane or ethylene. Collision-induced dissociation experiments in our laboratory and density functional calculations by Andrés and co-workers have shed light on the geometric structures of group V transition metal oxide cluster cations.[5,8,15,18] From the collision-induced dissociation experiments, density functional theory calculations, and knowledge of the stable oxidation states of vanadium, two different types of structural features might be present on $(V_2O_5)_n^+$ clusters that could result in the enhanced ability of these clusters to transfer an oxygen atom to ethane or ethylene. The first type of structural feature that is discussed is

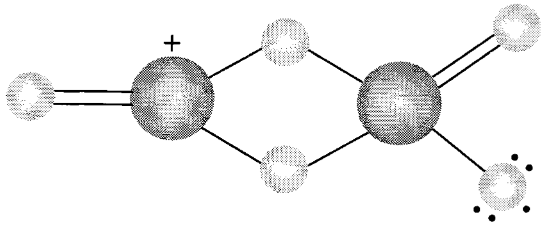

Figure 5. Possible oxygen centered radical structure of $(V_2O_5)^+$.

an oxygen centered radical with the extra electron present on one of the oxygen atoms of the $(V_2O_5)_n^+$ clusters and the second type of structural feature that is considered is the presence of a peroxo ligand on $(V_2O_5)_n^+$ clusters.

Neutral M_2O_5, where M is a group V transition metal, is a stable closed shell species. If it is assumed that oxygen is strictly a two electron acceptor where all of the oxygen atoms have a (−2) oxidation state and the positive charge is counted as an additional valence, then the oxidation states of the transition metal atoms in $M_2O_5^+$ would be (+5, +6), but as previously mentioned (+6) is not a stable oxidation state for group V transition metals. However, if one of the terminal oxygen atoms of $M_2O_5^+$ forms a single metal−oxygen bond and the oxygen atom has a (−1) oxidation state, then both of the metal atoms would be in the (+5) oxidation state. This type of structure, which is shown in Figure 5, is referred to as an oxygen centered radical. The dioxy bridged structure of $V_2O_5^+$ is used throughout this paper because density functional calculations have shown this structure to be 70 kJ/mol more stable than the single oxygen bridged structure.[19,20] Typically, the metal−oxygen bond lengths decrease from the neutral metal oxide cluster to the cationic metal cluster. However, elongation of a metal−oxygen bond frequently occurs upon ionization of a closed shell species to form a cationic oxygen centered radical.[21] Andrés and co-workers have performed systematic density functional calculations on $V_xO_y^{+/o}$ clusters.[18] It was determined from these DFT calculations that upon removal of an electron from neutral V_2O_5, one of the terminal vanadium−oxygen bonds lengthens from 1.585 to 1.701 Å, where the elongated vanadium−oxygen bond has single bond character and the oxygen atom is in the (−1) oxidation state. The spin density was also calculated and it was determined that the extra electron is located on the oxygen atom of the elongated vanadium−oxygen bond, which also indicates that $V_2O_5^+$ could be an oxygen centered radical. Additionally, Andrés and co-workers have performed density functional theory calculations on $Nb_xO_y^{+/o}$ clusters and found that the niobium−oxygen bond length increases from 1.779 Å in Nb_2O_5 to 1.790 Å in $Nb_2O_5^+$, which indicates that $Nb_2O_5^+$ could also be an oxygen centered radical.[22]

Because the density functional theory calculations by Andrés and co-workers indicate that the most stable structures that were calculated for $V_2O_5^+$ and $Nb_2O_5^+$ possess an elongated metal−oxygen bond, loss of atomic oxygen from these particular metal oxide clusters should occur easily during reactions with ethane and ethylene due to the presence of a weakened $M_2O_4{-}O^+$ bond. Additionally, this idea can be extrapolated to consider the clusters $V_4O_{10}^+$ and $V_6O_{15}^+$, which also show a significant oxygen transfer reaction during reactions with ethane and ethylene. These particular clusters were not calculated by Andrés and co-workers, but it is conceivable that $V_4O_{10}^+$ and $V_6O_{15}^+$ could also possess an elongated vanadium−oxygen bond and oxygen transfer from the cluster to ethane or ethylene might occur due to a relatively weak $(V_2O_5)_{n-1}V_2O_4{-}O^+$ bond strength, where $n = 2$ or 3. In fact, this type of behavior has been observed in the reactions of molybdenum oxide cluster cations with carbon monoxide and c-C_3H_6. Fialko et al. established that cationic clusters of the stoichiometry $(MoO_3)_n^+$ have a radical oxygen species in the (−1) oxidation state and an elongated $(MoO_3)_{n-1}MoO_2{-}O^+$ bond compared to neutral $(MoO_3)_n$.[23] During the reactions of $(MoO_3)_n^+$ with CO and c-C_3H_6, it was observed that loss of atomic oxygen occurs rather easily because of the weaker $(MoO_3)_{n-1}MoO_2{-}O^+$ bond strength. Because DFT calculations by Andrés and co-workers indicate that $(V_2O_5)_n^+$ clusters might be oxygen centered radicals, it is possible that loss of atomic oxygen observed in our experiments with ethane and ethylene might occur easily due to the presence of a relatively weak $(V_2O_5)_{n-1}V_2O_4{-}O^+$ bond, where $n = 1$, 2, or 3. Additionally, it is possible that $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ might be oxygen centered radicals similar to Figure 5. However, in accordance with the metal−oxygen bond trends described earlier the $(Nb_2O_5)_{n-1}Nb_2O_4{-}O^+$ and $(Ta_2O_5)_{n-1}Ta_2O_4{-}O^+$ bonds may not be weak enough to easily transfer an oxygen atom to the hydrocarbon, which might be the reason the oxygen transfer channel is either minor or nonexistent during reactions of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ with C_2 hydrocarbons.

Although the elongated and weakened vanadium−oxygen bond of an oxygen centered radical could explain why $(V_2O_5)_n^+$ clusters easily transfer an oxygen atom to C_2 hydrocarbons, the collision-induced dissociation results of $(V_2O_5)_n^+$, where $n =$ 2 or 3, do not seem to agree with this particular structure.[5] Additionally, the collision-induced dissociation of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$, where $n = 1$ or 2, also are not consistent with the presence of an elongated and weakened metal−oxygen bond that is associated with an oxygen centered radical.[8,15] If $(M_2O_5)_n^+$ clusters are actually oxygen centered radicals, then it is thought that atomic oxygen loss would be observed during collision-induced dissociation of $(M_2O_5)_n^+$ clusters. As previously stated, an atomic oxygen loss channel is only observed during collision-induced dissociation of $V_2O_5^+$ at $E_{CM} \geq 1$ eV.[5] Loss of atomic oxygen is not observed upon the collision of $V_4O_{10}^+$, $V_6O_{15}^+$, $Nb_2O_5^+$, $Nb_4O_{10}^+$, $Ta_2O_5^+$, or $Ta_4O_{10}^+$ with an inert gas at near thermal energy or at a center-of-mass energy in excess of 3 eV.[5,8,15] Therefore, it is concluded that only the collision-induced dissociation results of $V_2O_5^+$ seem to support the suggestion that $(M_2O_5)_n^+$ clusters are oxygen centered radicals with an elongated metal−oxygen bond. For this reason, other structural possibilities must be explored in addition to the oxygen centered radical in order to attempt to explain why oxygen transfer only occurs for $(V_2O_5)_n^+$ clusters during reactions with ethane and ethylene.

The collision-induced dissociation results of $(M_2O_5)_n^+$ indicate that the geometric structure of $(V_2O_5)_n^+$ clusters is different compared to $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ clusters. During collision-induced dissociation, $V_4O_{10}^+$ and $V_6O_{15}^+$ exhibit loss of molecular oxygen at near thermal energy and $V_2O_5^+$ lose molecular oxygen at $E_{CM} \geq 2$ eV, which implies the presence of O−O bonds in $(V_2O_5)_n^+$ clusters.[5] The clusters which lose molecular oxygen during collision-induced dissociation are referred to as oxygen-rich clusters and can be represented as $V_xO_y(O_2)^+$. In contrast, stoichiometrically equivalent niobium and tantalum oxide clusters, $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$, do not show loss of molecular oxygen during collision-induced dissociation experiments and therefore almost certainly do not possess O−O bonds.[8,15]

Figure 6 demonstrates the various ways in which oxygen can be bound to a transition metal.[24] Figure 6(a) shows an oxo complex, OMO, where the oxygen molecule is dissociatively bound to the transition metal, forming two separate metal−

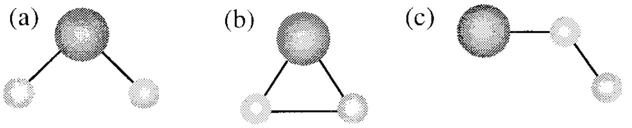

Figure 6. Structure of (a) oxo, (b) peroxo, and (c) superoxo dioxide isomers bound to a transition metal. The lines that represent the metal−oxygen bonds in this figure are not meant to describe the bond order associated with that particular bond. See text.

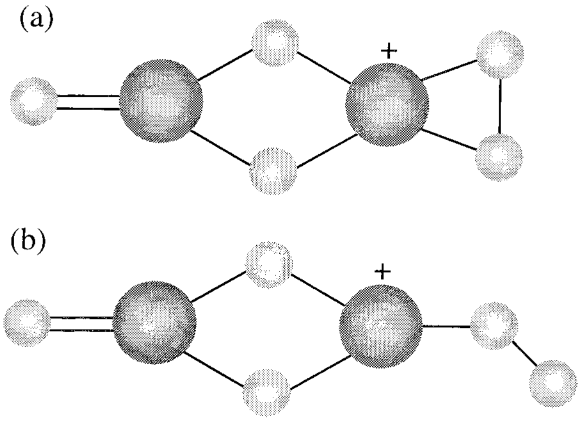

Figure 7. Possible (a) peroxo and (b) superoxo structure of $V_2O_5^+$.

oxygen bonds with no interaction between the two oxygen atoms. It is difficult to imagine that metal oxide clusters that possess only the type of metal−oxygen bonding shown in Figure 6(a) would lose an O_2 molecule during collision-induced dissociation because no O−O bonds are present. Presumably, the bonding shown in Figure 6(a) is the only type of bonding present in the terminal transition metal−oxygen bonds in $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ because these clusters do not show loss of molecular oxygen during collision-induced dissociation. The other types of bonding found in transition metal oxygen complexes are shown in Figures 6(b) and 6(c), where the oxygen atoms are bound associatively to the transition metal. The first possible type of structure that has an oxygen molecule associatively attached to the transition metal is a peroxo structure, $M(O_2)$, which is characterized as a triangular bidentate. In the peroxo structure shown in Figure 6(b) the π-bond of O_2 is broken and two covalent bonds to the transition metal are formed. The other type of structure where the oxygen molecule is associatively bound to the transition metal is called a superoxo structure, MOO, which is shown in Figure 6(c). For the superoxo system shown in Figure 6(c), one of the oxygen atoms of O_2 forms a covalent bond to the transition metal, whereas the other oxygen atom has a radical character. Therefore, it is evident that if either the peroxo or superoxo ligand is present on a metal oxide cluster, loss of molecular oxygen could occur easily during collision-induced dissociation.[25] Consequently, it is highly probable that the oxygen-rich group V transition metal oxide cluster cations that lose molecular oxygen during collision-induced dissociation, such as $(V_2O_5)_n^+$, have either a peroxo or superoxo ligand that is easily lost upon collision with an inert gas.

As stated earlier, if all of the terminal oxygen atoms of the $(V_2O_5)_n^+$ clusters were double bonds, then one vanadium atom would be in the (+6) oxidation state, which is not a stable oxidation state for vanadium, whereas the remaining vanadium atoms would be in the (+5) oxidation state. The presence of a peroxo ligand on $(V_2O_5)_n^+$ clusters, which is illustrated in Figure 7(a), would enable all of the vanadium atoms of the cluster to adopt oxidation states lower than (+6). If clusters with the stoichiometry $(V_2O_5)_n^+$ possess a peroxo group, then this would result in one vanadium atom in the (+4) oxidation state, while the other vanadium atoms present in the cluster would be pentavalent. It is evident from Figure 7(a) that this peroxo ligand also has the potential to result in facile O_2 loss during collision-induced dissociation. In fact, the presence of a peroxo ligand on $(V_2O_5)_n^+$ clusters might make them active toward oxygen transfer to ethane and ethylene because it has been found that peroxo complexes of early transition metals are active in olefin oxidation reactions.[26] Specifically, peroxovanadium complexes perform a variety of oxidation reactions, such as the transformation of alkenes to epoxides and of alkanes to alcohols.[27] Therefore, it is proposed that the presence of a peroxo group on gas phase $(V_2O_5)_n^+$ clusters might be necessary in order to observe oxygen transfer during reactions with ethane and ethylene. Because $(V_2O_5)_n^+$ clusters lose molecular oxygen during collision-induced dissociation, it is also possible that this cluster might have a superoxo ligand, which is shown in Figure 7(b). However, it is not believed that a superoxo ligand is present on $(V_2O_5)_n^+$ clusters because the vanadium atoms would be in oxidation states lower than (+5) and the vanadium atom with the attached superoxo structure would be coordinatively unsaturated. In fact, it has been determined that the binding in the superoxides is always weaker than that of the peroxides and will only occur if the peroxide ligand is blocked by other ligands, which is not the case for the $V_2O_5^+$ cluster.[28] Consequently, it is thought that the superoxo structure shown in Figure 7(b) would not be stable because the terminal oxygen atom of the superoxo group would favor bonding to an open coordination site on the vanadium atom to form a peroxo ligand rather than remaining a superoxo ligand. The collision-induced dissociation results of $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ suggest that these clusters are not oxygen-rich as they do not lose molecular oxygen upon collision with an inert gas.[8,15] This indicates that $(Nb_2O_5)_n^+$ and $(Ta_2O_5)_n^+$ clusters do not have O−O bonds and are not likely to possess a peroxo ligand, which might hinder them from exhibiting the oxygen transfer channel during reactions with ethane and ethylene if in fact the presence of a peroxo ligand is necessary for oxygen transfer to occur.

It is apparent from Tables 1 and 2 and from Figures 1 and 2 that none of the vanadium oxide clusters with an odd number of vanadium atoms display an oxygen transfer product during reactions with ethane and ethylene. The reactions of $V_3O_8^+$ and $V_5O_{13}^+$ with ethane and ethylene simply exhibit loss of molecular oxygen, a replacement reaction, and an association product. The clusters $V_3O_8^+$ and $V_5O_{13}^+$ are oxygen-rich clusters that lose molecular oxygen during collision-induced dissociation.[5] Therefore, it is believed that these clusters are $V_3O_6^+$ and $V_5O_{11}^+$ with molecular oxygen adsorbed onto the cluster surface. Additionally, $V_3O_8^+$ and $V_5O_{13}^+$ are the first clusters in their respective series to lose molecular oxygen upon collision with an inert gas, whereas the clusters of lower oxygen-to-metal ratio ($V_3O_{6,7}^+$ and $V_5O_{11,12}^+$) do not lose O_2 upon collision with an inert gas. It should also be mentioned at this time that $V_2O_5^+$, $V_4O_{10}^+$, and $V_6O_{15}^+$ are the first clusters in their respective series to lose molecular oxygen upon collision with an inert gas, whereas clusters of lower oxygen-to-metal ratio ($V_2O_{3,4}^+$, $V_4O_{8,9}^+$, and $V_6O_{13,14}^+$) do not lose O_2 upon collision with an inert gas. Andrés and co-workers have calculated various structures of $V_3O_6^+$ and found that the most stable structure is a six-membered ring with one terminal oxygen atom attached to each of the vanadium centers and three bridging oxygen atoms present in the ring structure.[18] This structure has the vanadium atoms in the (+4, +4, +5) oxidation states. If molecular oxygen

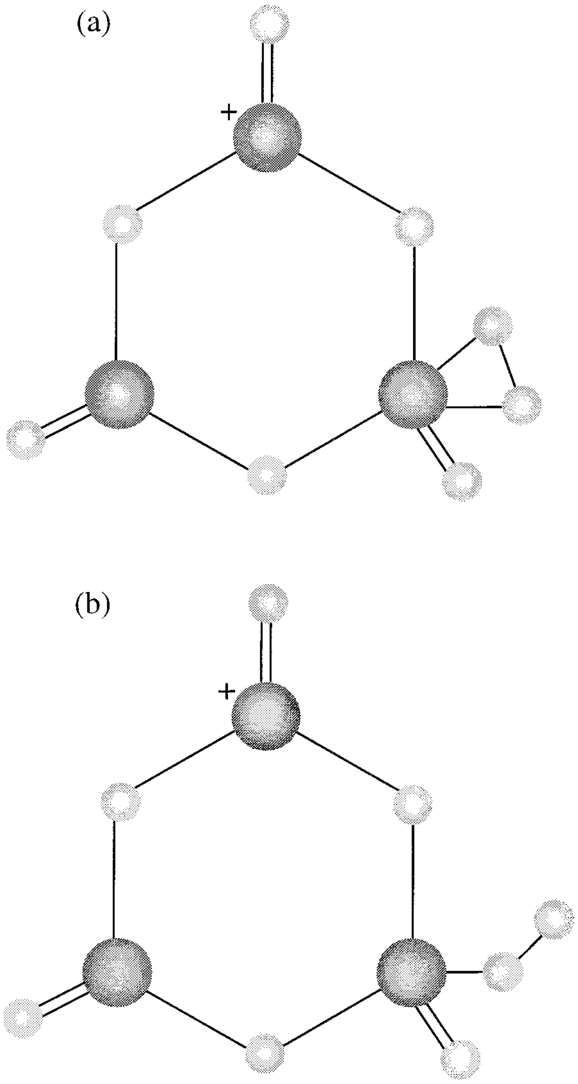

Figure 8. Possible (a) peroxo and (b) superoxo structure of $V_3O_8^+$.

is adsorbed onto $V_3O_6^+$ as a peroxo ligand, which is shown in Figure 8(a), the oxidation states of the vanadium atoms of $V_3O_8^+$ would be (+4, +5, +6). Also the vanadium atom that has the adsorbed peroxo structure will be coordinatively saturated. However, if molecular oxygen is adsorbed onto $V_3O_6^+$ as a superoxo ligand, which is shown in Figure 8(b), then vanadium atoms of $V_3O_8^+$ would be in the (+4, +5, +5) oxidation states. The superoxo structure seems more plausible for $V_3O_8^+$ compared to the peroxo structure because of the degree of coordinative saturation imposed by having a peroxo structure. Therefore, it is possible that oxygen-rich clusters with an odd number of vanadium atoms have molecular oxygen adsorbed on the cluster surface as a superoxo ligand.

It is postulated that the reason that oxygen transfer readily occurs during the reactions of $(V_2O_5)_n^+$ with ethane and ethylene might be due to the presence of a peroxo ligand. It is believed that a peroxo ligand could be present on $(V_2O_5)_n^+$ clusters because there would be an open coordination site for the triangular metallacycle to be formed. However, it is thought that a peroxo ligand is not present on vanadium oxide clusters with an odd number of vanadium atoms because there is only one open coordination site and one of the vanadium atoms would be in the (+6) oxidation state. Instead, it is postulated that oxygen-rich vanadium oxide clusters with an odd number of vanadium atoms have a superoxo ligand. Furthermore, it is not thought that $(Nb_2O_5)_n^+$ or $(Ta_2O_5)_n^+$ clusters have a peroxo ligand because these clusters do not lose molecular oxygen during collision-induced dissociation. Therefore, the vanadium oxide clusters with an odd number of vanadium atoms, $(Nb_2O_5)_n^+$, and $(Ta_2O_5)_n^+$ might not show oxygen transfer during reactions with ethane and ethylene because these clusters do not have a peroxo ligand.

One important discrepancy in the collision-induced dissociation results of $V_2O_5^+$ and the proposed peroxo structure must be addressed. As stated earlier, $V_2O_5^+$ loses a single oxygen atom during CID at $E_{CM} \geq 1$ eV and molecular oxygen is only lost from $V_2O_5^+$ during CID after the addition of $E_{CM} \geq 2$ eV.[5] However, it is thought that if there is a peroxo ligand present on the cluster that molecular oxygen would be lost easily, similar to $V_4O_{10}^+$ and $V_6O_{15}^+$ clusters, during collision-induced dissociation.[5] It is postulated that the positively charged vanadium atom in $V_2O_5^+$ draws electrons away from the O−O bond of the peroxo group and thereby weakens the O−O bond. This could create a structure where there is little interaction between the two oxygen atoms and might explain why the atomic oxygen loss channel is the major fragmentation pathway observed during CID of $V_2O_5^+$ as opposed to molecular oxygen loss. Furthermore, because $V_4O_{10}^+$ and $V_6O_{15}^+$ are larger than $V_2O_5^+$, it is possible that the positive charge is delocalized on the larger clusters and therefore does not weaken the O−O bond, which would explain why molecular oxygen is lost during CID.

To shed light on the role of charge state, the reactions of group V transition metal oxide anions with ethane and ethylene were also investigated. Collision-induced dissociation of vanadium oxide cluster anions in our laboratory has revealed that VO_4^-, $V_2O_6^-$, $V_3O_9^-$, $V_4O_{11}^-$, and $V_6O_{16}^-$ exhibit loss of atomic oxygen at a center of mass energy below 2 eV.[14] This indicates that atomic oxygen is loosely bound to these clusters and that they might be able to transfer an oxygen atom to a C_2 hydrocarbon. However, it was determined that $M_xO_y^-$ are completely unreactive toward ethane and ethylene, even though certain $M_xO_y^+$ did exhibit oxygen transfer and association channels. This demonstrates that the charge state of the cluster does have a dramatic effect on the reactivity of group V transition metal oxide cluster ions with ethane and ethylene. The lack of reactivity of metal oxide anions with C_2 hydrocarbons might indicate that the oxygen transfer reaction is dependent on cluster structure, such as the presence of a peroxo group or an oxygen centered radical. None of the vanadium oxide anions examined in this study lose molecular oxygen during collision-induced dissociation. Therefore, it is not thought that they possess O−O bonds and most likely do not have peroxo or superoxo ligands. These anion studies could indicate that the presence of a peroxo group is needed in order for oxygen transfer to the C_2 hydrocarbon to occur. However, it is also possible that $M_xO_y^-$ does not react with ethane and ethylene due to a decreased ability to polarize the C_2 hydrocarbon substrate compared to $M_xO_y^+$. The presence of positive charge may act to strengthen the interaction with the C_2 hydrocarbon, enhance the effect of electron withdrawal, and lower the activation barriers for reaction. However, the opposite effects are observed for metal oxide anions because the diffuse negative charge will reduce electron withdrawing effects and less strongly polarize the C_2 hydrocarbon. For this reason, a reaction complex might not form during reactions of metal oxide anion clusters with ethylene, which might be why association and oxygen transfer products are not observed.

There are three different mechanisms that are commonly used to describe the transfer of an oxygen atom from a gas phase or condensed phase metal oxygen complex to ethylene. The first mechanism involves a metallaoxetane intermediate, which is often used to describe oxygen transfer reactions in the condensed phase.[29] This metallaoxetane intermediate accounts for oxygen transfer from the gas-phase transition metal oxygen complex to ethylene and also for cleavage of the C═C bond of ethylene and has been proposed as the mechanism for several gas-phase reactions of metal oxygen complexes with ethylene and ethane.[30,31] The second type of mechanism proposed for an oxygen transfer reaction from a gas-phase transition metal oxygen complex to ethylene involves a carbocation intermediate structure.[21] The third type of mechanism that has been proposed for the oxygen transfer reaction from a condensed phase transition metal oxygen complex to ethylene involves the organic molecule interacting with the oxygen of instead of the transition metal of the transition metal oxide complex. Sharpless and co-workers suggest that oxygen transfer occurs by direct attack of the nucleophilic olefin on an electrophilic peroxo oxygen.[32] The transition state of this direct attack mechanism is a spiro structure, where the C−C bond is almost orthogonal to the plane formed by the peroxo group and the metal center. Density functional calculations and experimental data have revealed that the direct attack mechanism is preferred as significantly higher activation barriers were calculated for the insertion mechanism, where the olefin bonds to the metal center.[33] The mechanism of oxygen transfer from $(V_2O_5)_n^+$ clusters to ethane and ethylene and the identity of the oxygenated neutral hydrocarbon is not certain at this time. Therefore, theoretical calculations on the structures of $(V_2O_5)_n^+$ and the reactions of $(V_2O_5)_n^+$ with ethane and ethylene will be undertaken in order to provide insight into these concerns.

Conclusion

The reactions of group V transition metal oxide cluster ions with ethane and ethylene were investigated using a guided ion beam mass spectrometer. Vanadium oxide cluster cations of the specific stoichiometry $(V_2O_5)_n^+$ were found to be reactive toward oxygen transfer to the neutral hydrocarbon, whereas the corresponding vanadium oxide cluster anions were determined to be completely unreactive toward both association and oxygen transfer reactions. On the basis of this special behavior, we propose that $(V_2O_5)_n^+$ is a possible reactive center for the oxidation of ethane and ethylene. Additionally, this reaction pathway is minor or nonexistent in the case of reactions of ethane and ethylene with stoichiometrically equivalent niobium and tantalum oxide cluster cations. It was determined during these experiments of group V transition metal oxide cluster ions with C_2 hydrocarbons that the nature of the metal, the charge state, the cluster stoichiometry, and the geometric structure strongly influence the ability of the metal oxide cluster to transfer an oxygen atom to ethane and ethylene.

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