Reactions of Niobium and Tantalum Oxide Cluster Cations and Anions with *n*-Butane

K. A. Zemski, D. R. Justes, R. C. Bell, and A. W. Castleman, Jr.*

Departments of Chemistry and Physics, The Pennsylvania State University,
University Park, Pennsylvania 16802

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Reactions of niobium and tantalum oxide cluster cations ($M_xO_y^+$) and anions ($M_xO_y^-$) with *n*-butane (C_4H_{10}) are reported. The major reaction channels observed during the reaction of certain stoichiometric niobium and tantalum oxide cluster cations include association of *n*-butane ($M_xO_yC_4H_{10}^+$), C−C activation ($M_xO_yC_2H_4^+$), loss of an oxygen atom ($M_xO_{y-1}^+$), and dehydration ($M_xO_{y-1}C_4H_8^+$). Reactions of C_4H_{10} with oxygen-rich clusters are also reported herein and the major reaction channel of most of these oxygen-rich clusters involves a replacement reaction, where C_4H_{10} replaces an oxygen molecule. In addition, reactions of niobium and tantalum oxide anions ($M_xO_y^-$) with *n*-butane were also examined and it was established that the metal oxide cluster anions are unreactive toward this saturated hydrocarbon. The present study establishes the importance of the charge center, composition, size, and degree of coordinative saturation of the cluster on the reactivity with *n*-butane.

Introduction

Hydrocarbons, particularly alkanes, are one of the most abundant and inexpensive raw materials in the chemical industry. Therefore, chemical conversion of alkanes to more valuable, functionalized products represents an extremely important field of modern chemistry. However, due to the inert nature of saturated hydrocarbons, selective activation of alkane C−H and C−C bonds is quite a challenge and their use as starting materials in chemical processes is still rather limited.[1] Cleavage of C−C bonds by heterogeneous catalysts is particularly important to the petroleum industry since it is the central step in the breakdown of hydrocarbons into smaller molecules. However, the mechanism by which this process occurs is still under some debate and the low product selectivity observed with the current heterogeneous catalytic system is a significant drawback.[2] Consequently, a better understanding of the crucial mechanistic steps, a complete characterization of intermediates, and the determination of structure−reactivity relationships is of utmost importance in order to improve existing catalysts and develop new catalytic processes that will commence the chemical exploitation of natural gases and fuel feedstocks.

The issue of structure−reactivity relationships arises in many areas of heterogeneous catalytic chemistry. Surface experimental techniques provide information on atomic structure and composition of surfaces, but cannot directly probe the structure−reactivity relationship due to the variety of coordination sites present on surfaces.[3] However, the difficulty of surface inhomogeneity in understanding surface-reactivity relationships can be overcome by examining the reactivity of gas-phase transition metal oxide clusters. A metal oxide surface can be thought of as a collection of clusters of different sizes and isomers.[4] Therefore, gas-phase metal oxide clusters are regarded as the simplest model for the interaction of active sites on a transition metal oxide catalyst with organic molecules. The effect of composition, stoichiometry, size, charge state, and degree of coordinative saturation, which are among the most important factors affecting catalytic properties, can be examined by employing gas-phase techniques. These reaction products also provide valuable information about reaction intermediates and mechanisms. Therefore, gas-phase transition metal oxide clusters allow an excellent opportunity to study fundamental alkane activation reactions.

Numerous gas-phase studies on the reactivity of bare transition metal ions and monomeric metal oxide ions with hydrocarbons have been performed,[5−7] but there have been few gas-phase studies on the reactivity of metal oxide clusters. In our laboratory the reactivity of vanadium oxide cluster cations with C_4 hydrocarbons[8] and halogen-containing compounds[9−11] has been studied. Considering work from other laboratories, Zamaraev and co-workers have illustrated that there are striking similarities between reactions of methanol with gas-phase molybdenum oxide cluster cations and those taking place over real molybdenum oxide catalysts.[12] Finally, Rademann and co-workers have demonstrated that mass-selected bismuth oxide cluster cations in the gas phase can be reduced by propene in a manner similar to heterogeneous bismuth oxide catalysts.[13]

The results reported herein are of reactions of niobium and tantalum oxide cluster cations and anions with *n*-butane. One of the main reasons niobium oxide clusters were selected is because niobia catalysts have received much attention recently due to their catalytic activity in selective oxidation, hydrocarbon conversions, and polymerization reactions.[14] Conversely, tantalum oxides were chosen because of the paucity of information on the catalytic properties of this particular transition metal oxide.[15] Additionally, the reactions of vanadium oxide cluster cations with *n*-butane have been examined in our laboratory and were established to be relatively inert toward activating the C−C and C−H bonds of *n*-butane.[8] Therefore, these current studies were performed in order to examine the effect that different transition metals in the same group of the periodic table have in the activation of C−C and C−H bonds of saturated

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* Author to whom correspondence should be addressed.

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hydrocarbons and oxygen transfer from the cluster to the neutral hydrocarbon. Finally, the new fundamental insights gained from these gas-phase studies can provide information for the molecular engineering of group V metal oxide catalysts.

Experimental Section

A guided ion beam mass spectrometer coupled with a laser vaporization source, which has been described in detail previously,[16] is used to study the reactions of mass-selected niobium and tantalum oxide cluster ions with *n*-butane. Briefly, the second harmonic output of a Nd:YAG laser (5−26 mJ/pulse, 20 Hz) is focused onto the metal rod. The metal rod 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 surface, where plasma reactions occur and niobium or tantalum oxide clusters are produced. The clusters exit the source, where upon they are further cooled by supersonic expansion. They then 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 then enter the first quadrupole, where the ion of interest, $M_xO_y^{\pm}$, is selected from the cluster distribution. The selected cluster proceeds through a second set of electrostatic lenses into an octopole ion guide. A capacitance manometer (MKS) is used to monitor the pressure of *n*-butane 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 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 reaction pathways observed for niobium and tantalum oxide cluster cations with *n*-butane (C_4H_{10}) under thermal energy conditions include association of the hydrocarbon, oxygen transfer, dehydration, and C−C bond activation. It should be noted that these reactions were also carried out with deuterated *n*-butane in order to verify the identity of the reaction products. The metal oxide cluster cations, MO_{2-3}^+, $M_2O_{4-5}^+$, $M_3O_{7-8}^+$, $M_4O_{9-10}^+$, and $M_5O_{12-13}^+$, are referred to as stoichiometric clusters. Certain stoichiometric metal oxide clusters were found to be reactive toward oxygen transfer, dehydration, and C−C activation during reactions with *n*-butane. The clusters of higher oxygen content, MO_{4-5}^+, $M_2O_{6-8}^+$, $M_3O_9^+$, and $M_4O_{11}^+$, are referred to as oxygen-rich clusters because molecular oxygen is lost near thermal energies and under single collision conditions during collision-induced dissociation (CID) experiments.[17,18]

The results of the reactions of tantalum oxide cluster cations with *n*-butane under thermal energy conditions are shown in Table 1. All of the stoichiometric clusters, except $Ta_4O_{9-10}^+$, exhibit an association channel, $Ta_xO_yC_4H_{10}^+$. The major product for the reactions of TaO_2^+ and $Ta_2O_{4-5}^+$ with *n*-butane is activation of the C2−C3 bond, which is described as follows:

$$Ta_xO_y^+ + C_4H_{10} \rightarrow Ta_xO_yC_2H_4^+ + C_2H_6 \qquad (1)$$

TABLE 1: Reactions of $Nb_xO_y^+$ and $Ta_xO_y^+$ with 0.15 mTorr *n*-Butane

cluster (*x*,*y*)	$Nb_xO_y^+$ reaction products	$Ta_xO_y^+$ reaction products
(1,2)	$NbO_2C_2H_4^+$	$TaO_2CH_4^+$
	$NbOC_4H_8^+$	$TaO_2C_2H_4^+$
	$NbO_2C_4H_{10}^+$	$TaO_2C_3H_6^+$
		$TaO_2C_4H_{10}^+$
(1,3)	NR	$TaO_3C_4H_{10}^+$
(1,4)	- -	TaO_2^+
		$TaO_2C_4H_{10}^+$
(1,5)	- -	TaO_3^+
		$TaO_3C_4H_{10}^+$
(2,4)	$Nb_2O_4C_4H_{10}^+$	$Ta_2O_4CH_4^+$
		$Ta_2O_4C_2H_4^+$
		$Ta_2O_4C_3H_6^+$
		$Ta_2O_4C_4H_{10}^+$
(2,5)	$Nb_2O_4^+$	$Ta_2O_5CH_4^+$
	$Nb_2O_5C_2H_4^+$	$Ta_2O_5C_2H_4^+$
	$Nb_2O_4C_4H_{10}^+$	$Ta_2O_5C_3H_6^+$
	$Nb_2O_5C_4H_{10}^+$	$Ta_2O_5C_4H_{10}^+$
(2,6)	$Nb_2O_4^+$	$Ta_2O_4^+$
	$Nb_2O_6C_4H_{10}^+$	$Ta_2O_6C_4H_{10}^+$
(2,7)	$Nb_2O_5^+$	$Ta_2O_5^+$
	$Nb_2O_5C_4H_{10}^+$	$Ta_2O_5C_4H_{10}^+$
(2,8)	$Nb_2O_6^+$	$Ta_2O_6^+$
	$Nb_2O_6C_4H_{10}^+$	$Ta_2O_6C_4H_{10}^+$
(3,7)	$Nb_3O_7C_4H_{10}^+$	$Ta_3O_7C_4H_{10}^+$
(3,8)	$Nb_3O_7^+$	
	$Nb_3O_8C_4H_{10}^+$	$Ta_3O_8C_4H_{10}^+$
(3,9)	$Nb_3O_7^+$	$Ta_3O_7^+$
	$Nb_3O_7C_4H_{10}^+$	$Ta_3O_7C_4H_{10}^+$
(4,9)	NR	NR
(4,10)	$Nb_4O_9^+$	NR
(4,11)	$Nb_4O_9^+$	$Ta_4O_9^+$
(5,12)	$Nb_5O_{12}C_4H_{10}^+$	$Ta_5O_{12}C_4H_{10}^+$
(5,13)	$Nb_5O_{13}C_4H_{10}^+$	$Ta_5O_{13}C_4H_{10}^+$

It should be mentioned that the neutral products cannot be determined in our experimental apparatus because only ionic species are detected. Therefore, the most probable neutral reaction products are shown. There were also additional cracking products for TaO_2^+ and $Ta_2O_{4-5}^+$, which arose via reactions 2 and 3.

$$Ta_xO_y^+ + C_4H_{10} \rightarrow Ta_xO_yCH_4^+ + C_3H_6 \qquad (2)$$

$$\rightarrow Ta_xO_yC_3H_6^+ + CH_4 \qquad (3)$$

All of the oxygen-rich clusters, TaO_{4-5}^+, $Ta_2O_{6-8}^+$, $Ta_3O_9^+$, and $Ta_4O_{11}^+$ exhibited a molecular oxygen loss channel to form the more stable stoichiometric cluster, according to reaction 4.

$$Ta_xO_y^+ + C_4H_{10} \rightarrow Ta_xO_{y-2}^+ + O_2 + C_4H_{10} \qquad (4)$$

Additionally, TaO_{4-5}^+, $Ta_2O_{7-8}^+$, and $Ta_3O_9^+$ displayed a replacement reaction channel, which arose via reaction 5.

$$Ta_xO_y^+ + C_4H_{10} \rightarrow Ta_xO_{y-2}C_4H_{10}^+ + O_2 \qquad (5)$$

In addition to the reactivity studies of $Ta_xO_y^+$ with *n*-butane, the reactions of tantalum oxide cluster anions with *n*-butane have been explored in order to determine the effect of charge state on these reactions. Interestingly, the reactions of $Ta_xO_y^-$ with C_4H_{10} did not generate any observable reaction products.

The results of the reactions of niobium oxide clusters with *n*-butane under thermal energy conditions are also displayed in Table 1. All of the stoichiometric clusters, except NbO_3^+ and $Nb_4O_{9-10}^+$, exhibit an association channel to give the product $Nb_xO_yC_4H_{10}^+$. One of the major products for the reaction of NbO_2^+ and $Nb_2O_5^+$ with *n*-butane is activation of the C2−C3 bond, which is described by reaction 6.

$$Nb_xO_y^+ + C_4H_{10} \rightarrow Nb_xO_yC_2H_4^+ + C_2H_6 \qquad (6)$$

NbO_2^+ was the only cluster to display a dehydration product according to reaction 7.

$$NbO_2^+ + C_4H_{10} \rightarrow NbOC_4H_8^+ + H_2O \qquad (7)$$

During reactions of $Nb_2O_5^+$, $Nb_3O_8^+$, and $Nb_4O_{10}^+$ with *n*-butane, a weak atomic oxygen loss product is observed, which is described by reaction 8.

$$Nb_xO_y^+ + C_4H_{10} \rightarrow Nb_xO_{y-1}^+ + (C_4H_{10}O) \qquad (8)$$

Again it is noted that the identity of the neutral species formed during these reactions cannot be determined by our experimental apparatus 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 niobium oxide cluster to *n*-butane. The oxygen-rich clusters, $Nb_2O_{6-8}^+$, $Nb_3O_9^+$, and $Nb_4O_{11}^+$, exhibited a molecular oxygen loss channel to form the more stable stoichiometric cluster according to reaction 4. Additionally, $Nb_2O_{7-8}^+$ and $Nb_3O_9^+$ displayed a replacement reaction shown in reaction 5. Furthermore, the reactions of niobium oxide cluster anions with *n*-butane have been investigated. Similar to the reactions of tantalum oxide cluster anions with *n*-butane, the reactions of $Nb_xO_y^-$ with C_4H_{10} did not produce any observable reaction products.

Discussion

Branching ratios, which demonstrate how the product distribution changes as a function of pressure, were obtained for MO_2^+, $M_2O_{4-6}^+$, $M_3O_{7-9}^+$, $M_4O_{9-11}^+$, and $M_5O_{12-13}^+$ with *n*-butane. These branching ratios serve to reveal the differences in reactivity of niobium and tantalum cluster cations with *n*-butane. The branching ratios of $Nb_2O_5^+$, $Nb_3O_{7-9}^+$, $Nb_5O_{12-13}^+$, $Ta_2O_5^+$, $Ta_3O_{7-9}^+$, and $Ta_5O_{12-13}^+$ are shown in Figures 1−5. It is apparent from these branching ratios that many factors influence the reactivity of niobium and tantalum oxide clusters with *n*-butane, such as composition, charge state, size, and degree of coordinative saturation. The remainder of this discussion focuses on how these particular factors influence the reactivity of $Nb_xO_y^\pm$ and $Ta_xO_y^\pm$ with *n*-butane.

The reactivity and product distribution of group V transition metal oxide cations, $M_xO_y^+$, with *n*-butane are significantly affected by the identity of the metal. Previously, reactions of vanadium oxide cluster cations with *n*-butane have been examined in our laboratory.[8] Since vanadium, niobium, and tantalum occupy the same group of the periodic table, similar reactivities with *n*-butane may be anticipated, but there are some differences in the product distributions, which are shown in Figure 1. This figure displays the variation in reactivity of the mass-selected cluster, $M_2O_5^+$, with *n*-butane as the identity of M is changed from V to Nb to Ta. It is apparent from Figure 1 that the main reaction product of $V_2O_5^+$ with *n*-butane is $V_2O_4^+$, which is most likely an oxygen transfer product, whereas the primary reaction channel of $Nb_2O_5^+$ and $Ta_2O_5^+$ with *n*-butane is $M_2O_5C_2H_4^+$, which is a C−C activation channel. Schwarz and co-workers observed a similar trend during reactions of VO_2^+ and NbO_2^+ with ethylene.[19] The main products in the reaction of VO_2^+ with ethylene were VO^+ and neutral acetaldehyde. However, this oxygen transfer product was not observed during the reactions of NbO_2^+ with ethylene. Possible reasons for the anomalous reactivity in reactions of group V transition metal oxide clusters with *n*-butane are considered below.

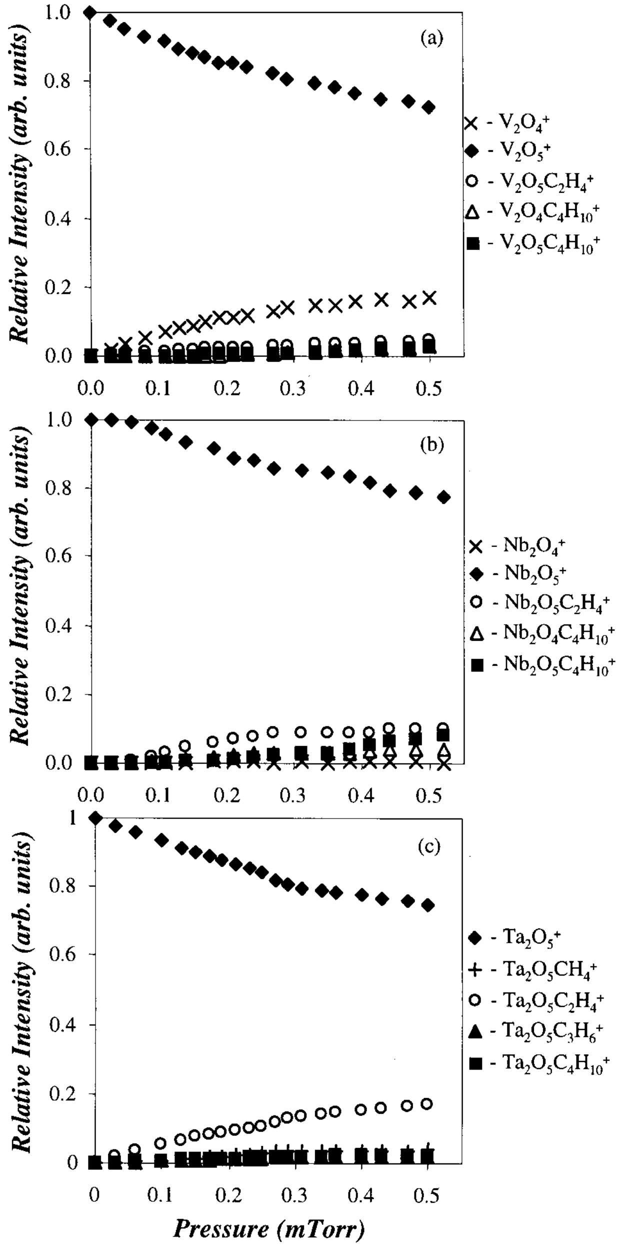

Figure 1. Branching ratios of (a) $V_2O_5^+$, (b) $Nb_2O_5^+$, and (c) $Ta_2O_5^+$ with *n*-butane. Note how the atomic oxygen loss channel decreases from $V_2O_5^+$ to $Ta_2O_5^+$ and how the cracking product increases from $V_2O_5^+$ to $Ta_2O_5^+$.

Oxygen transfer reaction products are of interest because oxidation is one of the main pathways for the activation of neutral hydrocarbons. In reactions of $V_xO_y^+$ with *n*-butane, it was determined that $V_2O_5^+$, $V_4O_{10}^+$, and $V_6O_{15}^+$ exhibit a significant atomic oxygen loss channel, $V_xO_{y-1}^+$, while $V_2O_6^+$, $V_3O_{7-8}^+$, $V_4O_9^+$, $V_5O_{11-12}^+$, $V_6O_{14}^+$, and $V_7O_{17-18}^+$ exhibit a weak $V_xO_{y-1}^+$ reaction channel.[8] In the current investigation $Nb_2O_5^+$, $Nb_3O_8^+$, and $Nb_4O_{10}^+$ exhibit a very weak atomic oxygen loss product according to reaction 8, while tantalum oxide cluster cations do not display an atomic oxygen loss channel. This is illustrated in the branching ratio of $M_2O_5^+$, where M is V, Nb, or Ta, with *n*-butane, which is shown in Figure 1. Prior collision-induced dissociation (CID) results of $V_xO_y^+$ using xenon as the target gas and $Nb_xO_y^+$ using krypton as the target gas demonstrate that these aforementioned clusters do not exhibit an atomic oxygen loss channel under single collision conditions at thermal energies.[8,18] Therefore, it is proposed that these reactions are due to oxygen transfer from the mass-selected cluster, $M_xO_y^+$, to *n*-butane, resulting in a single oxygen loss product, $M_xO_{y-1}^+$, and a neutral oxygenated *n*-butane molecule.

One of the key factors affecting oxidation reactions is the availability of a variety of stable oxidation states.[20] All of the group V transition metals have a strong tendency to be pentavalent, but vanadium can also form stable complexes with V^{2+}, V^{3+}, and V^{4+}. Since oxidation states lower than V^{5+} are stable for vanadium, this generally causes vanadium complexes to be better oxidizing agents than niobium or tantalum. It is likely that the availability of accessible oxidation states plays a role during the reactions of group V transition metal oxide cluster cations with *n*-butane because in order for an oxygen transfer product to be formed the metal oxide cluster must be reduced while *n*-butane is oxidized. Therefore, it is possible that the oxygen transfer product is the major product formed during reactions of certain $V_xO_y^+$ with *n*-butane because of the availability of various stable oxidation states. Likewise, it is possible that the oxygen transfer product is not the major reaction product during reactions of $Nb_xO_y^+$ and $Ta_xO_y^+$ with *n*-butane because these clusters are not as easily reduced due to the unavailability of a variety of stable oxidation states.

Another factor that plays a role in oxidation reactions is the strength of the metal−oxygen bond. It has been established that the hydrocarbon oxidation rate decreases with the strength of the metal−oxygen bond.[21] The bond strength of the V^+-O bond was determined to be 138 kcal/mol,[22] the Nb^+-O strength is 151 kcal/mol,[23] and the strength of the Ta^+-O was found to be 189 kcal/mol.[24] It is understood that the M^+-O bond strength in the group V transition metal oxide clusters examined in this current investigation will not be the same as the above-mentioned M^+-O bond strength values because the bond strength changes depending on the number of metal and oxygen atoms present in a cluster. For example, the value of the OV^+-O bond is 70.6 kcal/mol,[25] which is about 67 kcal/mol weaker than the V^+-O bond. It is highly probable that V^+-O bonds will be weaker than the stoichiometrically equivalent Nb^+-O and Ta^+-O bonds in these metal oxide clusters. Therefore, it is possible that vanadium oxide clusters could exhibit an oxygen transfer product during reactions with *n*-butane, where at least one V^+-O bond would be broken. Furthermore, the oxygen transfer product is not the major product during reactions of niobium and tantalum oxide cluster cations with *n*-butane, which might be attributed to the stronger M^+-O bonds.

Activation of C−C bonds of alkanes are of interest because it is the central step in the decomposition of hydrocarbons into smaller molecules in the petroleum industry. In reactions of $V_xO_y^+$ with *n*-butane, $V_2O_{4-5}^+$, $V_3O_{6-7}^+$, and $V_5O_{11-12}^+$ demonstrated a minor pathway for the C2−C3 activation reaction, $V_xO_yC_2H_4^+$.[8] However, in the current investigation NbO_2^+, $Nb_2O_5^+$, TaO_2^+, and $Ta_2O_{4-5}^+$ display significant C−C activation channels. This is apparent in the branching ratio of $M_2O_5^+$ with *n*-butane, which is shown in Figure 1. In order for a reaction to proceed favorably, the bonds formed during the reaction must be stronger than the bonds broken during the reaction. Accordingly, the thermochemistry of C−C insertion depends on the strength of the M−C bonds, the C−C binding energy of the hydrocarbon, and any energy barrier present in the reaction channel.[26] It is postulated that the reactions of niobium and tantalum oxide clusters with *n*-butane are metal-mediated reactions. DFT calculations by Sambrano et al. on niobium oxide cluster cations have indicated that the positive charge center is located on the niobium atoms of the cluster.[27] Since the positive charge center is located on the metal atom of niobium and tantalum oxide cluster cations, this enhances the M−C bond formation process. Therefore, it is thought that the strength of the M−C bonds may be an important factor in the reaction product distribution observed during the reactions of niobium and tantalum oxide cluster cations with *n*-butane. However, it should be mentioned that the possibility that O−C bond formation occurs cannot be discounted.

Typically, the second and third row transition metals are preferred for alkane activation because of the strong M−C bonds that are formed.[28] The lanthanide contraction causes the size of the *s* and *d* orbitals for second and third row transition metal atoms to be quite similar, which leads to better overlap of the *s* and *d* orbitals.[29] This results in the general trend of the second and third row transition metals possessing stronger M−ligand bonds than first row transition metals, which drives the C−C activation reaction. To the best of our knowledge, the only M−C bond dissociation energy that is reported in the literature for all of the group V transition metals is the M^+-CH_2 bond. The trend of the M^+-CH_2 bond dissociation energy values as reported in the literature show that the V^+-CH_2 is the weakest bond, while the Ta^+-CH_2 is the strongest bond.[30] Consequently, the M−C bond strength may be a key reason certain niobium and tantalum oxide cluster cations are able to activate the C−C bonds of *n*-butane. It is apparent from Table 1 and from previous results[8] that both $V_xO_y^+$ and $Nb_xO_y^+$ only activate the C2−C3 bond of *n*-butane, which is the weakest C−C bond of *n*-butane, to produce $M_xO_yC_2H_4^+$. Table 1 also shows that the reactions of $Ta_xO_y^+$ with *n*-butane are not selective in the sense that all of the C−C bonds are activated, resulting in the reaction products $Ta_xO_yCH_4^+$, $Ta_xO_yC_2H_4^+$, and $Ta_xO_yC_3H_6^+$. The presence of the products $Ta_xO_yCH_4^+$ and $Ta_xO_yC_3H_6^+$ may be explained by the stronger M−C bonds for tantalum compared to vanadium and niobium, which would result in a larger reaction exothermicity and in the activation of the stronger C−C bonds of *n*-butane.

One of the goals of a gas-phase chemist is to relate gas-phase chemistry to condensed phase chemistry. Recently in a review by Wachs et al. on group V transition metal oxide catalysts, it was revealed that active vanadia surface sites are primarily redox in nature.[15] In contrast, the active surface sites on niobia and tantala are primarily Lewis acid sites, which causes them to be less effective toward oxidation reactions. Our gas-phase studies reported herein are related to the results found on group V transition metal oxide surfaces, which is clearly exemplified in Figure 1. This figure reveals that the main reaction product of $V_2O_5^+$ with *n*-butane is $V_2O_4^+$, which is an oxygen transfer reaction and is comparable to the redox nature of vanadia catalyst surfaces. Conversely, the atomic oxygen loss channel is a minor reaction pathway during reactions of $Nb_2O_5^+$ with *n*-butane and is nonexistent during reactions with $Ta_2O_5^+$ with *n*-butane.

Another factor that has a dramatic effect on the reactivity of niobium and tantalum oxide cluster ions with *n*-butane is the charge state of the cluster. It has been reported herein that there are no observable reaction products formed during reactions of niobium and tantalum oxide cluster anions with *n*-butane, despite the fact that specific metal oxide cluster cations do display dehydration, C−C activation and association channels. The dependence of cluster reactivity on charge state has been explored previously. For example, Bondybey and co-workers established that platinum cluster cations react with methane at collision rates, whereas platinum cluster anions react more than a magnitude slower;[31] and they have reported that the overall

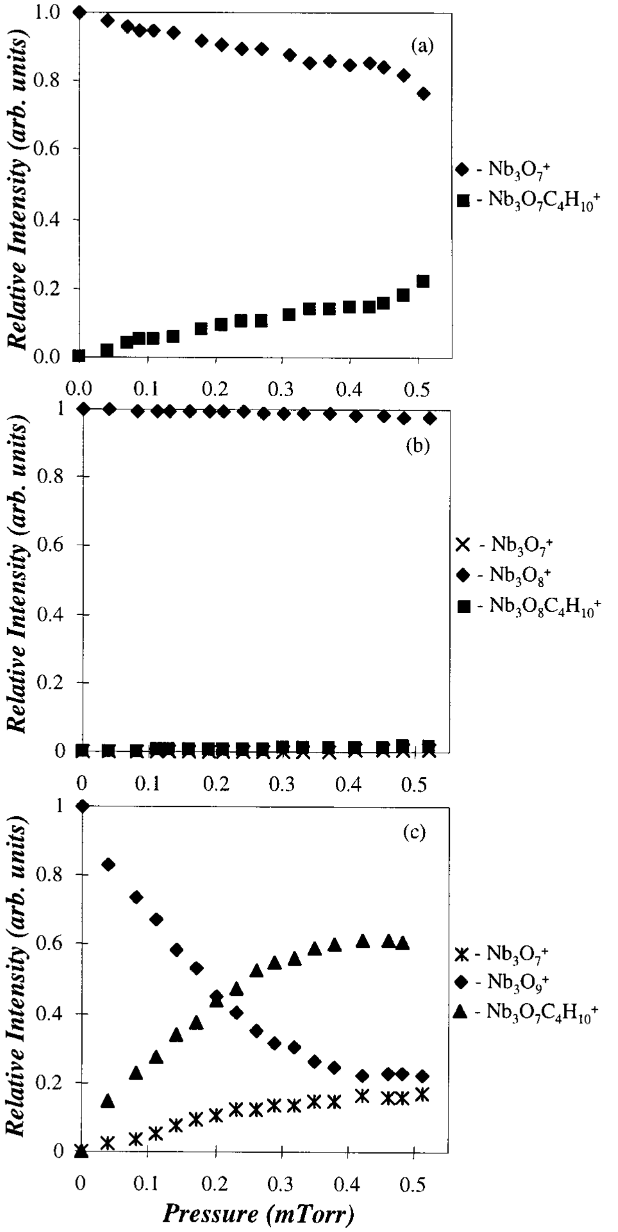

Figure 2. Branching ratios of (a) $Nb_3O_7^+$, (b) $Nb_3O_8^+$, and (c) $Nb_3O_9^+$ with *n*-butane.

reactivity of Nb_x^- is considerably smaller than the overall reactivity of Nb_x^+ with benzene.[32] Likewise, Kaldor and co-workers found that the reactivity of gold clusters with hydrogen, methane, and oxygen depends strongly on cluster charge state.[33] Additionally, Schröder et al. have indicated their preference for examining cationic metal oxides because neutral and anionic species are less likely to activate hydrocarbons.[34] This is because the cationic metal oxides, which behave as Lewis acids, initiate alkane activation by attacking the C−C bonds of the alkane.[35] Therefore, the C−C activation reactions that are observed herein during the reactions of $Nb_xO_y^+$ and $Ta_xO_y^+$ with *n*-butane may be due to the ability of $M_xO_y^+$ to polarize the *n*-butane substrate and activate it more easily than $M_xO_y^-$. It is thought that the presence of positive charge may act to strengthen the interaction with *n*-butane and enhance the effect of electron withdrawal. However, the opposite effects are observed for metal oxide anions because the negative charge will reduce electron withdrawing effects and less strongly polarize *n*-butane. These results indicate that the charge center has a very important effect on the reactivity. Additionally, it should be mentioned that experimental studies of oxidation reactions of hydrocarbons over metal oxide catalysts suggest that sites of anion vacancies are the catalytically active centers.[36]

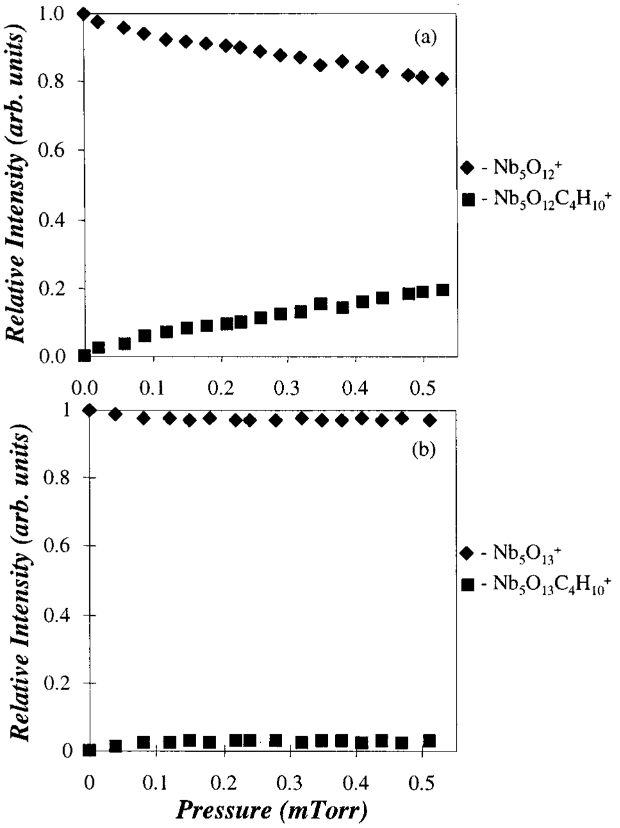

Figure 3. Branching ratios of (a) $Nb_5O_{12}^+$ and (b) $Nb_5O_{13}^+$ with *n*-butane.

The size of niobium and tantalum oxide cluster cations also appears to affect the reactivity of the clusters toward *n*-butane. Figure 6 shows that the $Nb_xO_yC_2H_4^+$ reaction channel is not present in reactions of *n*-butane with cationic metal oxide clusters containing $x \geq 3$ and that the association channel, $Nb_xO_yC_4H_{10}^+$, becomes the preferred reaction pathway when $x \geq 3$. A similar trend is also observed in the reactions of $Ta_xO_y^+$ with *n*-butane. It should be mentioned that the association product can be either a molecularly or dissociatively adsorbed *n*-butane molecule. There are several possible explanations why the reaction product distribution of larger $Nb_xO_y^+$ and $Ta_xO_y^+$ clusters seem to indicate that the larger clusters are not reactive toward activation of the C−C bonds of *n*-butane. It has been proposed herein that the charge state of the metal oxide cluster plays a considerable role in the reaction pathways that are observed. It is suggested that the positive charge is more localized on smaller clusters because it can be concentrated on fewer metal atoms. In contrast, the positive charge is more delocalized for the larger clusters because they possess more metal atoms. Consequently, this could result in the smaller metal oxide cluster cations strongly polarizing the bonds of *n*-butane and thereby being able to activate the C−C bonds of *n*-butane. However, this is not the only possible explanation as to why the product distributions of the larger niobium and tantalum oxide cluster cations seem to suggest that they are not reactive toward activating the C−C bonds of *n*-butane. Although, it is also likely that larger metal oxide cluster cations are able to activate *n*-butane, the larger size of the clusters may also allow for association of the neutral products formed during reactions

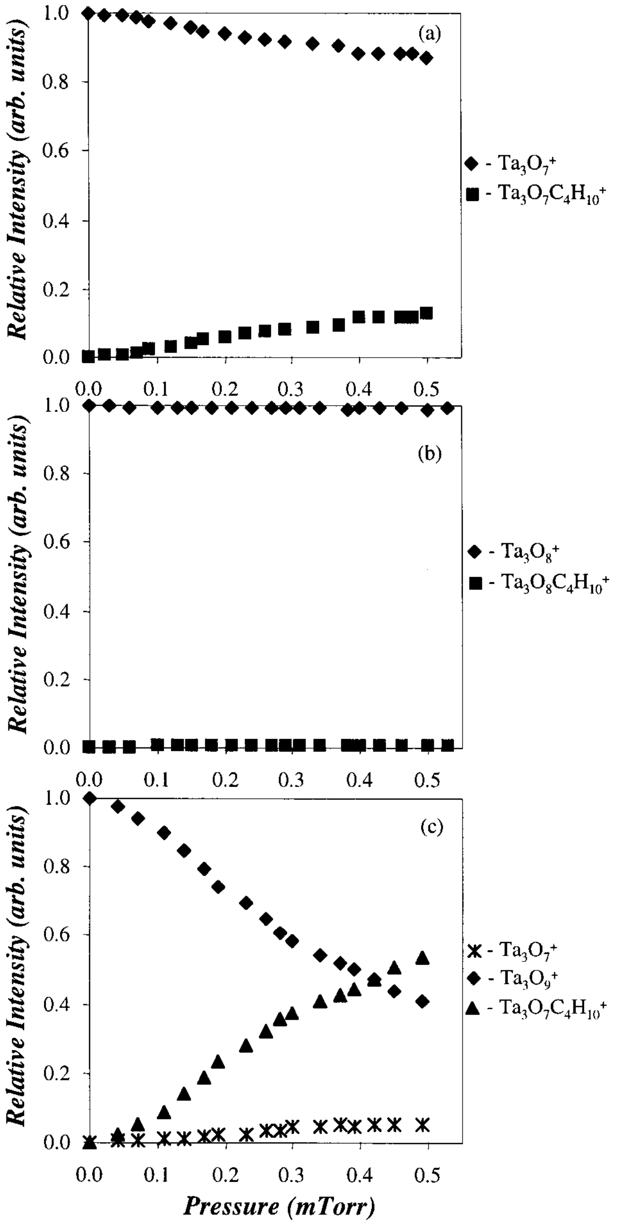

Figure 4. Branching ratios of (a) $Ta_3O_7^+$, (b) $Ta_3O_8^+$, and (c) $Ta_3O_9^+$ with *n*-butane.

with *n*-butane. In other words, it is possible that *n*-butane is dissociatively adsorbed as a pair of ethylene and ethane adsorbates on the larger clusters. This point is illustrated in Figure 6. Figure 6a shows that the C−C activation channel, $Nb_xO_yC_2H_4^+$, is only observed for the clusters NbO_2^+ and $Nb_2O_5^+$ and Figure 6b indicates that the clusters $Nb_3O_7^+$ and $Nb_5O_{12}^+$ display a strong reaction channel that corresponds to the ion mass of $Nb_xO_yC_4H_{10}^+$ compared to the other clusters studied. Therefore, it seems probable that the $Nb_xO_yC_2H_4^+$ product is not observed for $Nb_3O_7^+$ and $Nb_5O_{12}^+$ because the larger size of the metal oxide clusters allows for the adsorption of all of the reaction products onto the cluster and therefore results in a strong reaction channel with an ion mass corresponding to $Nb_xO_yC_4H_{10}^+$, which could be either molecularly or dissociatively adsorbed *n*-butane. Another possible reason that the larger metal oxide cluster cations studied did not exhibit C−C activation products is that the larger clusters have more degrees of freedom to distribute excess energy, consequently the dissociation of *n*-butane may not occur.

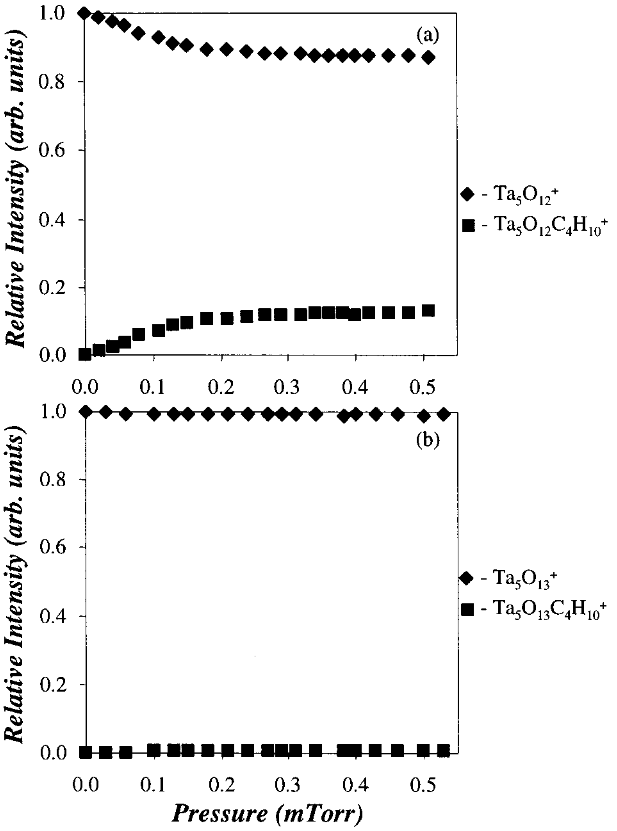

Figure 5. Branching ratios of (a) $Ta_5O_{12}^+$ and (b) $Ta_5O_{13}^+$ with *n*-butane.

Another factor that influences the reactivity of niobium and tantalum oxide cluster cations with *n*-butane is the degree of coordinative saturation of the cluster.[37] The degree of coordinative saturation is important because only a limited number of ligands can be within bonding distance of the metal oxide cluster due to steric and electronic reasons. Russell and coworkers have determined that the reactivity of metal carbonyl clusters can be related to the degree of coordinative unsaturation because the more open coordination sites present on a cluster, the higher the rate for ion−molecule reactions.[38] Likewise, coordinative unsaturation is an important factor in organometallic and heterogeneous catalysis and it has been determined in these types of studies that C−C bond activation requires a high degree of coordinative unsaturation.[39,40] The effect of coordinative saturation on the reactions of niobium and tantalum oxide cluster cations with *n*-butane can be observed in Figures 2−5. It is apparent from Figures 2 through 5 that the presence of an extra oxygen atom significantly changes the extent to which the cluster can associate *n*-butane. Typically, coordinatively unsaturated sites are responsible for the adsorption of reactant molecules. Therefore, it is possible that the addition of an oxygen atom onto $M_3O_7^+$ or $M_5O_{12}^+$ to form $M_3O_8^+$ or $M_5O_{13}^+$ causes the reaction site and charge center of the cluster to be sterically hindered, which alters the reactivity of the cluster.

The presence of oxo ligands on group V transition metal oxide cluster cations, $M_xO_y^+$, also seems to greatly influence the reactivity of these clusters compared to bare group V transition metal clusters, M_x^+. Freiser and co-workers investigated reactions of Nb^+ and Ta^+ with *n*-butane and the major reaction products observed were $MC_4H_4^+$ and $MC_4H_6^+$.[41] Additionally, Yang and co-workers probed the reactivities of Nb_x^+ with *n*-butane and established that the products observed were due to dehydrogenation reactions.[42] The product distribution ob-

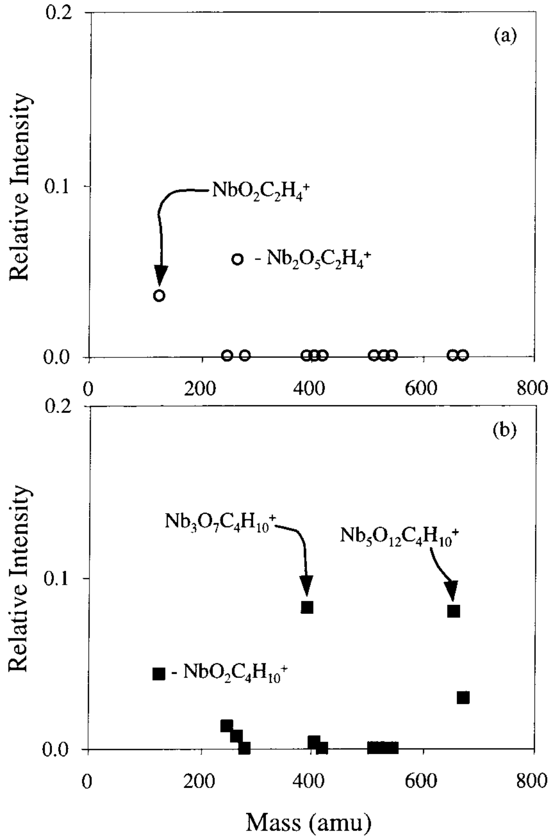

Figure 6. Branching ratio of the (a) the cracking product, $Nb_xO_yC_2H_4^+$, and (b) association product, $Nb_xO_yC_4H_{10}^+$, with 0.15 mTorr of *n*-butane. Note the general dependence on cluster size in these product distributions.

served during the reactions of $Nb_xO_y^+$ and $Ta_xO_y^+$ with *n*-butane in the current investigation is quite different because the major products are C2−C3 activation, $M_xO_yC_2H_4^+$, and association, $M_xO_yC_4H_{10}^+$, with no evidence of dehydrogenation occurring. The effect of oxo ligands on gas-phase reactions has been investigated previously. Cornehl et al. observed that upon addition of an oxygen ligand to lanthanide cations, the behavior toward 1,3-butadiene changes dramatically.[43] Additionally, McElvany and co-workers established that Mo^+ and MoO^+ were found to yield products that are the result of C−H activation, but MoO_2^+ is capable of inserting into C−C bonds of small alkanes.[44] Furthermore, Beauchamp and co-workers similarly found that the number of oxo ligands has a striking effect on the chemistry of osmium oxide cluster cations.[45] Therefore, the differences in the product distributions of bare group V transition metal cluster cations[41,42] compared to niobium and tantalum oxide cluster cations with *n*-butane may be attributed in part to the presence of oxo ligands. It is thought that the electronegativity of the oxygen atom increases the effective charge on the metal and therefore the Lewis acidity of the reactant ion, which may facilitate the C−C activation reactions that are observed herein.

The major reaction channel of oxygen-rich niobium and tantalum oxide cluster cations, MO_{4-5}^+, $M_2O_{6-8}^+$, $M_3O_9^+$, and $M_4O_{11}^+$, is loss of molecular oxygen to form stoichiometric clusters during reactions with *n*-butane, according to reaction 4. The molecular oxygen loss channel most likely results from a collision-induced dissociation (CID) process because these clusters exhibit loss of O_2 during CID experiments at thermal energies.[17,18] Previously, it has been proposed that these oxygen-rich clusters are stoichiometric clusters with a chemisorbed O_2 molecule. Most of the stoichiometric fragment products then proceed to associate *n*-butane onto the cluster. In addition, $M_2O_6^+$ displayed an association channel, $M_2O_6C_4H_{10}^+$. The branching ratios of $Nb_3O_9^+$ and $Ta_3O_9^+$ with *n*-butane are shown in Figures 2c and 4c. It is apparent from these figures that the major reaction channel is a replacement reaction, where the O_2 is replaced by a *n*-butane molecule and is in agreement with the earlier conjecture.

Conclusions

The reactivities of niobium and tantalum oxide cluster ions with *n*-butane were investigated using a guided ion beam mass spectrometer. Certain niobium and tantalum oxide cluster cations were found to be reactive toward activating the C−C bonds of *n*-butane, whereas the corresponding metal oxide cluster anions were determined to be completely unreactive. The extent to which $Nb_xO_y^+$ and $Ta_xO_y^+$ activate the C−C bonds of *n*-butane depends on the composition, charge state, size of the cluster, and degree of coordinative saturation. In the case of reactions of $Nb_xO_y^+$ with *n*-butane, the reactions were selective in terms of only activating the C2−C3 bond of *n*-butane. However, reactions of $Ta_xO_y^+$ with *n*-butane did not display selectivity in terms of which C−C bonds of *n*-butane are activated. Finally, similarities were observed between these gas-phase studies and condensed phase studies over group V metal oxide catalysts because vanadium oxide clusters were determined to be more likely to transfer an oxygen atom to *n*-butane compared to the niobium and tantalum oxide clusters.

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