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Reactions of Tantalum Oxide Cluster Cations with 1-Butene, 1,3-Butadiene, and Benzene

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Branching ratios for the reactions of 1-butene, 1,3-butadiene, and benzene with stoichiometric tantalum oxide clusters (TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_{7-8}^+$) are reported. The major reaction product for most of the clusters is cracking of the C2−C3 bond of 1-butene and 1,3-butadiene to produce $Ta_xO_yC_2H_4^+$. Additionally, $Ta_2O_4^+$ was the most reactive cluster toward cracking the C2−C3 bond of both 1-butene and 1,3-butadiene. For a majority of these clusters there were additional cracking channels to produce $Ta_xO_yCH_3^+$ and $Ta_xO_yC_3H_z^+$, where $z = 5-6$, which occur under multiple collision conditions for 1-butene and 1,3-butadiene. Under multiple collision conditions, TaO_2^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ exhibited the reaction channels of $Ta_xO_yC_5H_9^+$ and $Ta_xO_yC_6H_{10}^+$ when reacted with 1-butene. In reactions with 1,3-butadiene, secondary reaction channels of $Ta_xO_yC_5H_7^+$ and $Ta_xO_yC_6H_8^+$ were also observed for TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$. Additionally, under multiple collision conditions, TaO_2^+ and $Ta_2O_4^+$ also displayed reaction channels of $Ta_xO_yC_7H_9^+$ and $Ta_xO_yC_8H_{10}^+$. Reactions of most of the stoichiometric tantalum oxide clusters with benzene showed a cracking channel forming $Ta_xO_yC_4H_4^+$ and a dehydration channel to form $Ta_xO_{y-1}C_6H_4^+$. The most reactive cluster toward cracking benzene was $Ta_3O_8^+$, and the most reactive cluster toward the dehydration reaction was TaO_2^+. Reactions of the aforementioned unsaturated hydrocarbons with oxygen-rich clusters (TaO_{4-5}^+, $Ta_2O_{6-7}^+$, and $Ta_3O_{9-10}^+$) are also reported. The major reaction channel of most of these clusters involves loss of molecular oxygen to form the smaller, more stable stoichiometric clusters, which then proceed to react with or associate the hydrocarbon gas.

Introduction

Transition metal oxides are widely used as heterogeneous catalysts and catalytic supports in many industrial processes. For example, vanadium oxides form a group of industrially important catalysts for the selective oxidation of hydrocarbons.[1−3] Despite the extensive use of transition metal oxide catalysts, there is a lack of fundamental understanding of the complicated processes that occur on a metal oxide surface during catalytic processes. Specifically, a complete understanding of the complex relationship between the local structure and reactivity of the metal oxide and the mechanisms by which these catalysts function has not yet been established.

The surface structure of bulk transition metal oxides can be viewed as an assemblage of clusters of different sizes and structures. Additionally, surface bonds tend to have clusterlike properties.[4,5] Therefore, a novel approach to addressing the incomplete understanding of heterogeneous catalysis is to study the reactivities of gas-phase transition metal oxide clusters. Surface techniques, such as solid state NMR, extended X-ray absorption fine structure, and X-ray photoelectron spectroscopy, have provided information on atomic structure and composition of surfaces of metal oxides. However, in the gas phase different oxidation states, stoichiometries, sizes, and charge states can be selected in order to determine what effects these factors have on catalytic behavior. The gas-phase reaction products provide valuable information about reaction intermediates, reaction mechanisms, and the relationship between cluster structure and reactivity. Therefore, through gas-phase studies an understanding of transition metal oxide catalysts can be achieved at the molecular level, which can ultimately find use in designing more effective catalysts.

Developing methods to activate C−C and C−H bonds in hydrocarbons is one of the most important research efforts in catalytic chemistry. For this reason there have been many gas-phase studies on the reactivities of bare transition metal ions (M^+) and monomeric metal oxide ions (MO^+) with hydrocarbons,[6−8] but there have been few gas-phase studies on transition metal oxide clusters. The reactivities of vanadium oxide clusters have been thoroughly studied with various hydrocarbons, such as 1,3-butadiene, 1-butene, and *n*-butane,[9] and halogen-containing compounds, such as 1,1,1-trifluoroethane and hexafluoroethane,[10] difluoromethane,[11] and carbon tetrachloride.[12] Cursory studies on niobium oxide clusters with benzene, 1,3-butadiene, and acetone have also been performed.[13] Schwarz and coworkers have recently studied the reactivities of MO_2^+ (M = Ti, V, Zr, Nb) with small saturated hydrocarbons, such as methane, ethane, and propane.[14] Finally, Zamaraev and coworkers have shown that there are similarities between interactions of methanol with $Mo_xO_y^+$ ions in the gas phase and reactions of methanol over real molybdenum/oxygen catalysts in the condensed phase.[15]

The results reported herein are of reactions of tantalum oxide clusters with unsaturated hydrocarbon gases, such as 1-butene, 1,3-butadiene, and benzene. The main reason tantalum oxide clusters were chosen as the metal oxide system of interest is due to the paucity of information on the catalytic properties of bulk tantalum oxides. Preliminary condensed phase studies on tantalum oxides have shown some intriguing catalytic properties. Ushikubo et al. compared the catalytic activity of hydrated niobium and tantalum oxides with reactions such as the esterification of methacrylic acid with methanol, the alkylation of benzene with ethene, and the isomerization of 1-butene.[16]

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Hydrated tantalum oxides were found to be more effective than hydrated niobium oxides at catalyzing the aforementioned reactions for two reasons. First, hydrated tantalum oxide has a greater number of surface acidic sites compared to hydrated niobium oxide. Second, the acidic sites on the surface of hydrated tantalum oxide are stronger than those of hydrated niobium oxide. Additional studies by Ushikubo et al. have demonstrated that silica-supported tantalum oxides are able to efficiently catalyze the vapor-phase Beckmann rearrangement[17] and the vapor-phase decomposition of methyl *tert*-butyl ether.[18] These studies on the catalytic properties of condensed-phase tantalum oxides indicate that it is an intriguing system to examine in the gas phase.

Experimental Section

A triple quadrupole mass spectrometer coupled with a laser vaporization source, which has been described in detail previously,[19,20] is used to study the reactivities of tantalum oxide cluster cations with various unsaturated hydrocarbons. Briefly, the second harmonic output of a Nd:YAG laser (5−20 mJ/pulse, 20 Hz) is focused onto a tantalum 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. 10%) over the ablated surface, where plasma reactions occur and tantalum oxide clusters are produced. The clusters exit the source, whereupon 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, $Ta_xO_y^+$, is selected from the cluster distribution. The selected cluster then proceeds through a second set of electrostatic lenses into the second quadrupole. This quadrupole is operated in the rf-only mode and is used as either a reaction or collision cell. The translational energy of the tantalum oxide clusters is kept to a minimum by applying a ground potential to the entrance plate of the second quadrupole so that only thermal ions enter into the reaction region. A capacitance manometer (MKS) is used to monitor the pressure of the gas in the second quadrupole. After the reactions occur in the second quadrupole, the product ions exit and are guided by a third set of electrostatic lenses into the third 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

Preliminary results of the reactions of tantalum oxide clusters with 0.15−0.25 mTorr of 1,3-butadiene, 1-butene, and benzene have been reported.[21] Herein more complete findings of the reactions of tantalum oxide clusters with these unsaturated hydrocarbons at pressures varying from 0.03 to 0.65 mTorr are reported. Single collision conditions occur below 0.10 mTorr for this system currently under examination. The reaction pathways observed for the tantalum oxide clusters with 1,3-butadiene (C_4H_6), 1-butene (C_4H_8), and benzene (C_6H_6) include association of the hydrocarbon, oxygen transfer, cracking, and dehydration. The clusters of higher oxygen content, TaO_{4-5}^+, $Ta_2O_{6-7}^+$, and $Ta_3O_{9-10}^+$, will be referred to as oxygen-rich clusters because during collision-induced dissociation (CID) experiments they lose molecular oxygen near thermal energies and under single collision conditions.[21] The remaining tantalum oxide clusters, TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_{7-8}^+$, will be referred to as stoichiometric clusters. Most of the stoichiometric clusters were found to be reactive toward cracking the unsaturated hydrocarbons to some extent. Branching ratios, which show how the relative intensity of the reaction products change with pressure, were obtained for the stoichiometric clusters to aid in comparing the differences in reactivity from cluster to cluster. Reactions of the oxygen-rich clusters with 1-butene, 1,3-butadiene, and benzene are also addressed herein. One of the major reactions that oxygen-rich clusters undergo is loss of an O_2 molecule to form the stoichiometric clusters, which then proceed to either react with or to associate the hydrocarbon gas.

The results of the reactions of tantalum oxide clusters with 1-butene are shown in Table 1. Column *a* in Table 1 represents the product intensity of the individual reaction channels with respect to the other peaks in that particular spectrum, and column *b* represents the product intensity of the individual products with respect to all of the other cluster reactions studied. All of the stoichiometric clusters exhibit an association channel to give $Ta_xO_yC_4H_8^+$. The major product for the reactions of TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ with 1-butene is cracking of the C2−C3 bond, which is described as follows:

$$Ta_xO_y^+ + C_4H_8 \rightarrow Ta_xO_yC_2H_4^+ + C_2H_4 \qquad (1)$$

It should be noted that we do not know the identity of the neutral products of these reactions because we cannot detect them in our apparatus. There were also additional cracking products for TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$, which arose via reactions 2 and 3.

$$Ta_xO_y^+ + C_4H_8 \rightarrow Ta_xO_yCH_3^+ + C_3H_5 \qquad (2)$$

$$\rightarrow Ta_xO_yC_3H_6^+ + CH_2 \qquad (3)$$

Under multiple collision conditions, TaO_2^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ exhibited the reaction channels of $Ta_xO_yC_5H_9^+$ and $Ta_xO_yC_6H_{10}^+$, which will be referred to as secondary reaction products throughout this paper. TaO_3^+ and $Ta_2O_{5-6}^+$ exhibited an atomic oxygen loss channel to form TaO_2^+ and $Ta_2O_{4-5}^+$, respectively. All of the oxygen-rich clusters, $TaO_{y\geq 4}^+$, $Ta_2O_{y\geq 6}^+$, and $Ta_3O_{y\geq 9}^+$, exhibited a molecular oxygen loss channel to form the more stable stoichiometric clusters, which is most likely a CID process, according to reaction 4. The stoichiometric cluster formed in reaction 4 then proceeds to exhibit a 1-butene association channel.

$$Ta_xO_y^+ + C_4H_8 \rightarrow Ta_xO_{y-2}^+ + O_2 + C_4H_8 \qquad (4)$$

Figures 1−3 show the branching ratios for TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ with 1-butene. TaO_3^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ all exhibit typical behavior, where the relative intensity of the selected ion steadily decreases and the relative intensity of each of the products steadily increases with increasing pressure. However, TaO_2^+ and $Ta_2O_4^+$ both show a C2−C3 cracking product, which is signified by the dotted line, that exhibits an increase in relative intensity followed by a decrease in relative intensity as the pressure of 1-butene is increased in the second quadrupole. This will be referred to as uncharacteristic branching ratio behavior. By comparing these branching ratios, it is apparent that the reactivities of the selected clusters vary greatly.

Table 1 also shows the results for the reactions of tantalum oxide clusters with 1,3-butadiene. All of the stoichiometric clusters displayed an association channel to give $Ta_xO_yC_4H_6^+$. The major product of the reactions of TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and

TABLE 1: Results of Tantalum Oxide Cluster Cations ($Ta_xO_y^+$) with 0.17 mTorr of 1-Butene, 1,3-Butadiene, and Benzene

	1-butene			1,3-butadiene			benzene		
cluster (*x*,*y*)	*a*	*b*		*a*	*b*		*a*	*b*	
(1,2)	W	C	$TaO_2CH_3^+$	S	A	$TaO_2C_2H_4^+$	W	C	$TaO_2C_4H_4^+$
	S	A	$TaO_2C_2H_4^+$	W	C	$TaO_2C_3H_5^+$	M	B	$TaOC_6H_4^+$
	M	C	$TaO_2C_3H_6^+$	D	A	$TaO_2C_4H_6^+$	D	A	$TaO_2C_6H_6^+$
	D	A	$TaO_2C_4H_8^+$	M	B	$TaO_2C_5H_7^+$			
	W	C	$TaO_2C_5H_9^+$	M	A	$TaO_2C_6H_8^+$			
	M	C	$TaO_2C_6H_{10}^+$	W	B	$TaO_2C_7H_9^+$			
				W	B	$TaO_2C_8H_{10}^+$			
(1,3)	W	C	TaO_2^+	W	C	TaO_2^+	W	C	$TaO_2C_6H_4^+$
	M	C	$TaO_2C_2H_2^+$	M	C	$TaO_2C_2H_4^+$	D	A	$TaO_3C_6H_6^+$
	M	B	$TaO_2C_3H_6^+$	M	C	$TaO_3C_2H_4^+$			
	W	C	$TaO_3C_2H_4^+$	M	B	$TaO_2C_4H_6^+$			
	D	B	$TaO_2C_4H_8^+$	W	C	$TaO_2C_5H_7^+$			
	S	B	$TaO_3C_4H_8^+$	D	A	$TaO_3C_4H_6^+$			
				W	C	$TaO_2C_6H_8^+$			
(1,4)	W	C	TaO_2^+	W	C	TaO_2^+	M	C	TaO_2^+
	M	C	$TaO_2C_2H_4^+$	M	B	$TaO_2C_2H_4^+$	W	C	$TaO_2C_4H_4^+$
	D	B	$TaO_2C_4H_8^+$	W	C	$TaO_2C_3H_4^+$	D	A	$TaO_2C_6H_6^+$
				D	B	$TaO_2C_4H_6^+$			
(1,5)	M	B	TaO_3^+	W	B	TaO_3^+	M	B	TaO_3^+
	D	A	$TaO_3C_4H_8^+$	D	A	$TaO_3C_4H_6^+$	D	A	$TaO_3C_6H_6^+$
(2,4)	M	B	$Ta_2O_4CH_3^+$	W	C	$Ta_2O_4CH_3^+$	W	C	$Ta_2O_4C_4H_4^+$
	D	A	$Ta_2O_4C_2H_4^+$	D	A	$Ta_2O_4C_2H_4^+$	W	C	$Ta_2O_3C_6H_4^+$
	M	B	$Ta_2O_4C_3H_6^+$	W	C	$Ta_2O_4C_3H_5^+$	D	A	$Ta_2O_4C_6H_6^+$
	M	B	$Ta_2O_4C_4H_8^+$	M	B	$Ta_2O_4C_4H_6^+$	W	C	$Ta_2O_4C_{12}H_{12}^+$
	W	C	$Ta_2O_4C_5H_9^+$	W	C	$Ta_2O_4C_5H_7^+$			
	W	C	$Ta_2O_4C_6H_{10}^+$	M	C	$Ta_2O_4C_6H_8^+$			
				W	C	$Ta_2O_4C_7H_9^+$			
				W	C	$Ta_2O_4C_8H_{10}^+$			
(2,5)	W	C	$Ta_2O_4^+$	W	C	$Ta_2O_4^+$	M	B	$Ta_2O_5C_4H_4^+$
	W	C	$Ta_2O_5CH_3^+$	W	C	$Ta_2O_4C_2H_4^+$	W	C	$Ta_2O_4C_6H_4^+$
	D	B	$Ta_2O_5C_2H_4^+$	D	B	$Ta_2O_5C_2H_4^+$	D	A	$Ta_2O_5C_6H_6^+$
	W	C	$Ta_2O_5C_3H_6^+$	M	C	$Ta_2O_4C_4H_6^+$	W	C	$Ta_2O_5C_{12}H_{12}^+$
	W	C	$Ta_2O_5C_4H_8^+$	W	C	$Ta_2O_5C_3H_5^+$			
				M	B	$Ta_2O_5C_4H_6^+$			
				W	C	$Ta_2O_4C_6H_8^+$			
				W	C	$Ta_2O_5C_6H_8^+$			
(2,6)	W	C	$Ta_2O_4^+$	W	C	$Ta_2O_4^+$	W	C	$Ta_2O_4^+$
	D	B	$Ta_2O_5^+$	D	B	$Ta_2O_5^+$	M	B	$Ta_2O_5^+$
	M	B	$Ta_2O_5C_2H_4^+$	M	B	$Ta_2O_4C_4H_6^+$	M	B	$Ta_2O_4C_4H_4^+$
	W	C	$Ta_2O_5C_4H_8^+$	M	C	$Ta_2O_5C_4H_6^+$	W	C	$Ta_2O_5C_4H_4^+$
				W	C	$Ta_2O_6C_4H_6^+$	W	C	$Ta_2O_4C_6H_6^+$
							W	C	$Ta_2O_5C_6H_6^+$
							D	A	$Ta_2O_6C_6H_6^+$
(2,7)	D	C	$Ta_2O_5^+$	D	B	$Ta_2O_5^+$	W	C	$Ta_2O_5^+$
	W	C	$Ta_2O_5C_4H_8^+$	M	B	$Ta_2O_5C_4H_6^+$	W	C	$Ta_2O_5C_4H_4^+$
							D	B	$Ta_2O_5C_6H_6^+$
							W	C	$Ta_2O_7C_6H_6^+$
(3,7)	M	B	$Ta_3O_7CH_3^+$	W	C	$Ta_3O_7CH_3^+$	D	A	$Ta_3O_7C_6H_6^+$
	M	B	$Ta_3O_7C_2H_4^+$	S	A	$Ta_3O_7C_2H_4^+$			
	M	C	$Ta_3O_7C_3H_6^+$	W	C	$Ta_3O_7C_3H_5^+$			
	D	A	$Ta_3O_7C_4H_8^+$	D	A	$Ta_3O_7C_4H_6^+$			
	W	C	$Ta_3O_7C_5H_9^+$	W	C	$Ta_3O_7C_5H_7^+$			
	W	C	$Ta_3O_7C_6H_{10}^+$	W	C	$Ta_3O_7C_6H_8^+$			
(3,8)	D	B	$Ta_3O_8C_4H_8^+$	D	B	$Ta_3O_8C_4H_6^+$	W	C	$Ta_3O_7C_4H_2^+$
							D	B	$Ta_3O_8C_4H_4^+$
							M	C	$Ta_3O_7C_6H_4^+$
							M	B	$Ta_3O_8C_6H_6^+$
(3,9)	W	C	$Ta_3O_7^+$	W	C	$Ta_3O_7^+$	W	C	$Ta_3O_7^+$
	D	A	$Ta_3O_7C_4H_8^+$	D	A	$Ta_3O_7C_4H_6^+$	D	A	$Ta_3O_7C_6H_6^+$
							W	C	$Ta_3O_9C_6H_6^+$
(3,10)	W	C	$Ta_3O_8^+$	D	C	$Ta_3O_8^+$	W	C	$Ta_3O_8^+$
	D	B	$Ta_3O_8C_4H_8^+$	M	B	$Ta_3O_8C_4H_6^+$	M	B	$Ta_3O_8C_4H_4^+$
							W	C	$Ta_3O_7C_6H_4^+$
							D	B	$Ta_3O_8C_6H_6^+$

[a] This column represents the product intensity with respect to the other peaks in that particular spectrum with each product marked as dominant (D), strong (S), moderate (M), or weak (W). [b] This column represents the product intensity with respect to all of the cluster reactions studied with each product marked as strong (A), moderate (B), or weak (C).

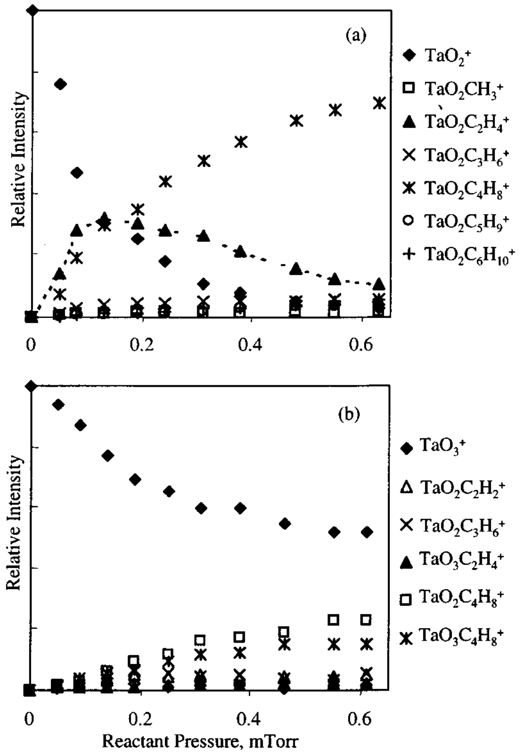

Figure 1. Relative product branching ratios for the reactions of 1-butene with (a) TaO_2^+ and (b) TaO_3^+. The uncharacteristic branching ratio behavior is indicated by the dotted line in (a). Please note that in (b) the product TaO_2^+ has been excluded because of the low intensity of this product.

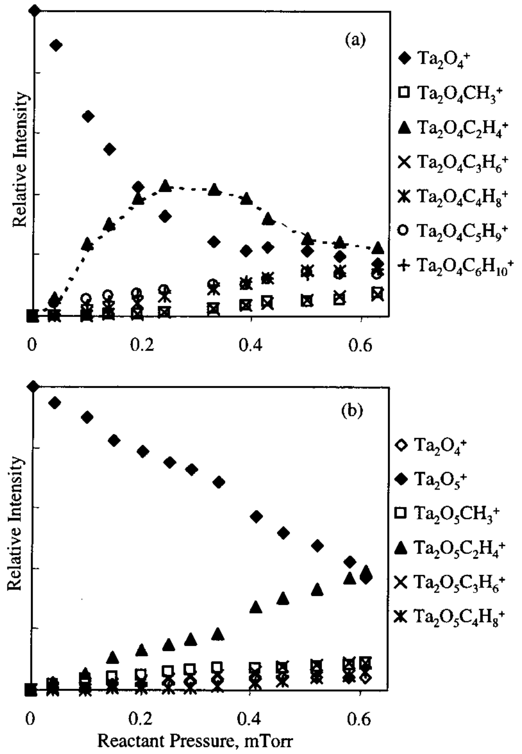

Figure 2. Relative product branching ratios for the reactions of 1-butene with (a) $Ta_2O_4^+$ and (b) $Ta_2O_5^+$. The uncharacteristic branching ratio behavior is indicated by the dotted line in (a).

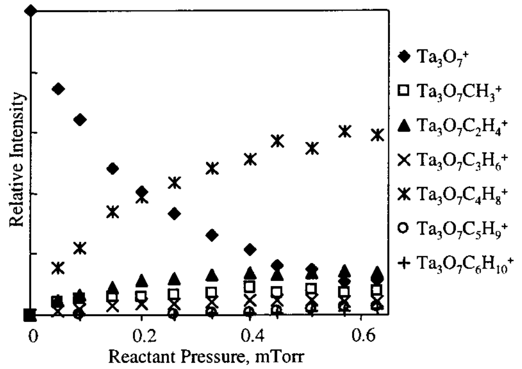

Figure 3. Relative product branching ratios for the reaction of 1-butene with $Ta_3O_7^+$.

$Ta_3O_7^+$ with 1,3-butadiene is cracking of the C2–C3 bond, according to reaction 5. There was also an additional cracking

$$Ta_xO_y^+ + C_4H_6 \rightarrow Ta_xO_yC_2H_4^+ + C_2H_2 \qquad (5)$$

product for TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$, which is described as

$$Ta_xO_y^+ + C_4H_6 \rightarrow Ta_xO_yC_3H_4^+ + CH \qquad (6)$$

Furthermore, $Ta_2O_4^+$ and $Ta_3O_7^+$ both show another cracking product, which is demonstrated as

$$Ta_xO_y^+ + C_4H_6 \rightarrow Ta_xO_yCH_3^+ + C_3H_3 \qquad (7)$$

Under multiple collision conditions, secondary reaction channels of $Ta_xO_yC_5H_7^+$ and $Ta_xO_yC_6H_8^+$ were also observed for TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$. Under multiple collision conditions, TaO_2^+ and $Ta_2O_4^+$ also displayed additional channels of $Ta_xO_yC_7H_9^+$ and $Ta_xO_yC_8H_{10}^+$. TaO_3^+ and $Ta_2O_{5-6}^+$ demonstrated an atomic oxygen loss channel to form TaO_2^+ and $Ta_2O_{4-5}^+$. The oxygen-rich clusters exhibited a molecular oxygen loss channel, similar to reaction 4. The stoichiometric cluster then proceeded to display a 1,3-butadiene association channel. Figures 4–6 display the branching ratios of TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ with 1,3-butadiene. The dotted line shows the uncharacteristic branching ratio behavior in the relative intensity of the C2–C3 cracking product, which was also observed for reactions of TaO_2^+ and $Ta_2O_4^+$ with 1-butene.

Finally, Table 1 shows the results of the reactions of tantalum oxide clusters with benzene. All of the stoichiometric clusters displayed an association channel to give $Ta_xO_yC_6H_6^+$. Under single collision conditions, TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_8^+$ with benzene displayed a cracking channel, which is shown in reaction 8. TaO_2^+, $Ta_2O_{4-6}^+$, and $Ta_3O_8^+$ showed dehydration

$$Ta_xO_y^+ + C_6H_6 \rightarrow Ta_xO_yC_4H_4^+ + C_2H_2 \qquad (8)$$

under single collision conditions, which is described as

$$Ta_xO_y^+ + C_6H_6 \rightarrow Ta_xO_{y-1}C_6H_4^+ + H_2O \qquad (9)$$

The reaction channel $Ta_3O_7C_4H_2^+$ was observed during reactions of $Ta_3O_8^+$ with benzene. TaO_2^+ and $Ta_2O_{4-5}^+$ also exhibited double association of benzene to give $Ta_xO_yC_{12}H_{12}^+$. There were also additional products for TaO_2^+ and $Ta_2O_4^+$ under multiple collision conditions, which correspond to reaction channels of $Ta_xO_yC_{10}H_{10}^+$ and $Ta_xO_{y-1}C_{12}H_{10}^+$. $Ta_2O_6^+$ showed an atomic oxygen loss channel. The oxygen-rich clusters exhibited a molecular oxygen loss channel, which is similar to reaction 4, to form stoichiometric clusters that further reacted to form benzene association products. Figures 7–9 display the branching ratios of TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_{7-8}^+$ with benzene. The

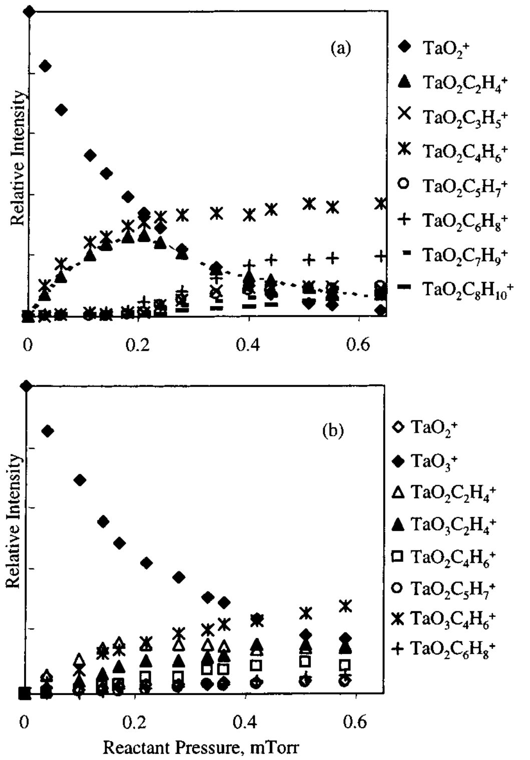

Figure 4. Relative product branching ratios for the reactions of 1,3-butadiene with (a) TaO_2^+ and (b) TaO_3^+. The uncharacteristic branching ratio behavior is indicated by the dotted line in (a).

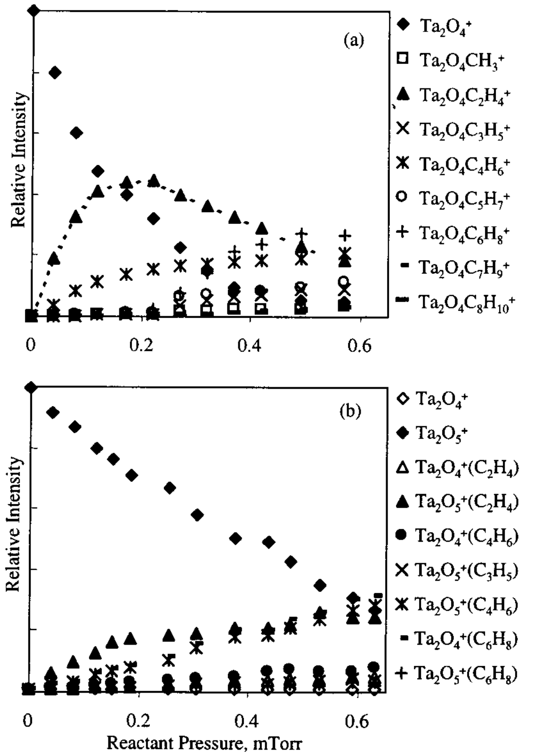

Figure 5. Relative product branching ratios for the reactions of 1,3-butadiene with (a) $Ta_2O_4^+$ and (b) $Ta_2O_5^+$. The uncharacteristic branching ratio behavior is indicated by the dotted line in (a).

benzene association channels of $Ta_2O_{4-5}^+$ also displayed uncharacteristic branching ratio behavior.

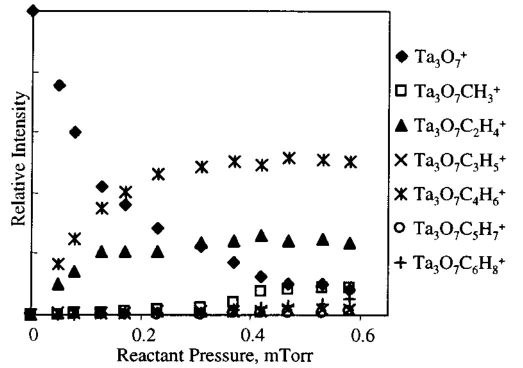

Figure 6. Relative product branching ratios for the reaction of 1,3-butadiene with $Ta_3O_7^+$.

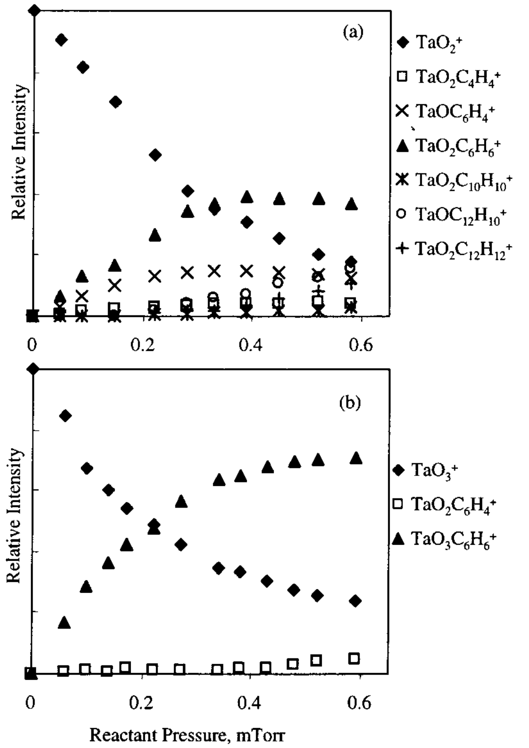

Figure 7. Relative product branching ratios for the reactions of benzene with (a) TaO_2^+ and (b) TaO_3^+.

Discussion

The branching ratios of the reactions of stoichiometric tantalum oxide cluster cations with 1-butene, 1,3-butadiene, and benzene, which serve to reveal the differences in reactivity of the clusters, are shown in Figures 1−9. The dotted lines in Figures 1a, 2a, 4a, 5a, 8a, and 8b indicate uncharacteristic branching ratio behavior, which has been defined as a product channel that exhibits an increase in relative intensity followed by a decrease in relative intensity as the pressure of reactant gas in the second quadrupole is increased. This effect is present under multiple collision conditions in the reaction cell. The results of pressure dependence studies at a fixed pressure of 0.15 mTorr of 1-butene is shown in Figure 10. This experiment was performed on TaO_2^+ in order to determine if this behavior is due to the increase of pressure in the reactant cell. These studies were performed in such a way that the partial pressure of 1-butene remains constant in the reactant cell, but the actual pressure in the second quadrupole is increased by sequentially diluting 1-butene with krypton. Krypton was used because it is fairly close in mass to 1-butene and because it is inert. It is evident from the pressure dependence studies that the relative intensities of the products remained constant with increasing pressure in the reaction cell. Additionally, similar results were obtained for a partial pressure of 0.25 mTorr of 1-butene.

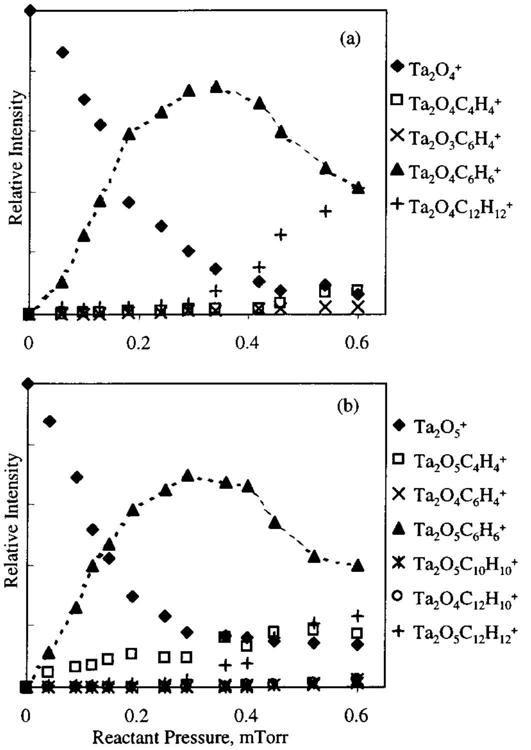

Figure 8. Relative product branching ratios for the reactions of benzene with (a) $Ta_2O_4^+$ and (b) $Ta_2O_5^+$. The uncharacteristic branching ratio behavior is indicated by the dotted lines.

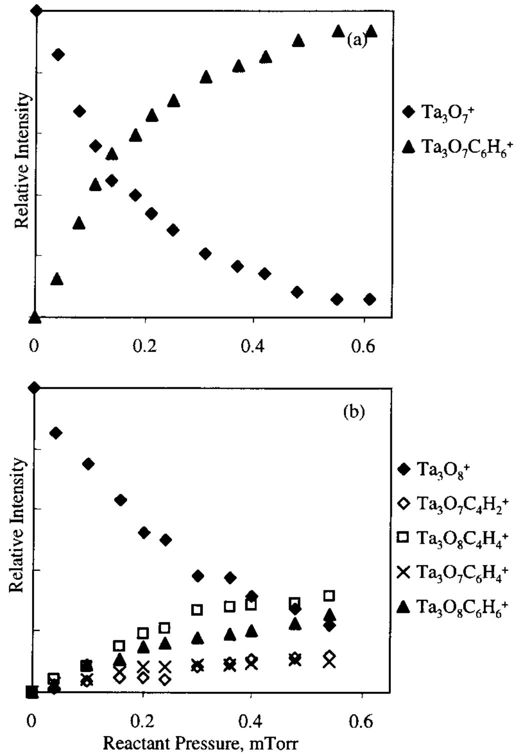

Figure 9. Relative product branching ratios for the reactions of benzene with (a) $Ta_3O_7^+$ and (b) $Ta_3O_8^+$.

Therefore, these experiments suggest that the uncharacteristic branching ratio behavior is not due to increased pressure inside the second quadrupole.

It is postulated that the uncharacteristic branching ratio behavior for reactions of TaO_2^+ and $Ta_2O_4^+$ with 1-butene and 1,3-butadiene could be due to the $Ta_xO_yC_2H_4^+$ reaction product undergoing additional reactions at higher pressures to form secondary reaction products. Figure 1a shows the uncharacteristic branching ratio behavior for the C2−C3 cracking product of TaO_2^+ with 1-butene. In this particular figure, the decrease in relative intensity of $TaO_2C_2H_4^+$ corresponds to an increase in relative intensity of $TaO_2C_4H_8^+$. It is possible that $TaO_2C_4H_8^+$ is a secondary reaction product according to

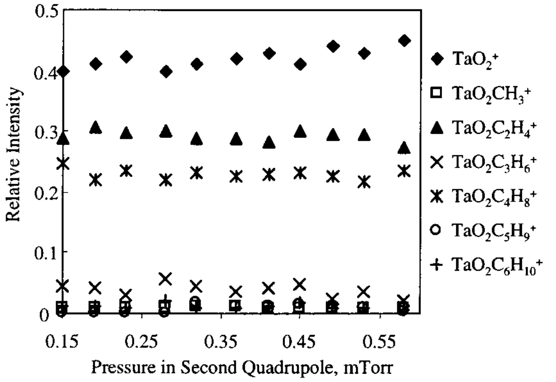

Figure 10. Pressure dependence study of TaO_2^+ with 0.15 mTorr of 1-butene.

$$TaO_2C_2H_4^+ + C_4H_8 \rightarrow TaO_2(C_2H_4)_2^+ + C_2H_4 \quad (10)$$

However, our present experimental apparatus cannot be used to distinguish between molecular and dissociative adsorption reactions on a cluster. Reaction 10 would account for the decrease in relative intensity of $TaO_2C_2H_4^+$ and an increase in the relative intensity of $TaO_2C_4H_8^+$ that is observed in Figure 1a. Figure 2a shows the uncharacteristic branching ratio behavior for the C2−C3 cracking product of $Ta_2O_4^+$ and 1-butene. In this case the uncharacteristic branching ratio behavior corresponds with a leveling off of the selected peak relative intensity at ~0.35 mTorr, along with an increase in relative intensity of secondary reaction products. Therefore, the uncharacteristic branching ratio behavior is most likely the result of further reaction of the $Ta_2O_4C_2H_4^+$ product at higher pressures to form various secondary reaction products.

For Figures 4a and 5a, the uncharacteristic branching ratio behavior is also observed for the C2−C3 cracking channel in reactions of TaO_2^+ and $Ta_2O_4^+$ with 1,3-butadiene. In the case of Figure 4a, the decrease in relative intensity of $TaO_2C_2H_4^+$ starting at ~0.21 mTorr corresponds to a significant increase in relative intensity of the $TaO_2C_6H_8^+$ channel and a moderate increase in relative intensity of other secondary reaction products. At higher pressures $TaO_2C_2H_4^+$ possibly undergoes further reactions according to reaction 11. This would account

$$Ta_xO_yC_2H_4^+ + C_4H_6 \rightarrow Ta_xO_yC_6H_8^+ + H_2 \quad (11)$$

for the considerable increase in relative intensity of the $TaO_2C_6H_8^+$ product. It is also surmised that the other secondary reaction products contribute to the decrease in relative intensity of $TaO_2C_2H_4^+$. In Figure 5a, the decrease in relative intensity of $Ta_2O_4C_2H_4^+$ corresponds to a significant increase in the relative intensity of $Ta_2O_4C_6H_8^+$ beginning at ~0.25 mTorr. Using the same reasoning for TaO_2^+, at higher pressures the $Ta_2O_4C_2H_4^+$ product may undergo further reactions according to reaction 11, which would cause a rise in the relative intensity of $Ta_2O_4C_6H_8^+$ along with the decrease of $Ta_2O_4C_2H_4^+$. Additionally, we have shown in Figure 10 that the uncharacteristic branching ratio behavior is not due to increased pressure in the cell, but is due to an increase in the concentration of reactant gas. These results also suggest that the uncharacteristic branching ratio behavior is due to the appearance of additional products at higher concentrations of reactant gas. In conclusion, it is believed that the uncharacteristic branching ratio behavior is exclusively observed for TaO_2^+ and $Ta_2O_4^+$ because these clusters are quite reactive toward cleaving the C2−C3 bond of 1-butene and 1,3-butadiene and the $Ta_xO_yC_2H_4^+$ reaction products are still rather reactive themselves, which contributes to the production of secondary reaction products.

Upon examination of the branching ratios of tantalum oxides with benzene, Figures 7−9, it is apparent that the tantalum oxide clusters have different reactivities. In Figure 8 the uncharacteristic branching ratio behavior is observed for the reaction channel, $Ta_xO_yC_6H_6^+$, of $Ta_2O_{4-5}^+$ with benzene. Upon examination of this figure, it is clear that the decrease in relative intensity of $Ta_2O_{4-5}C_6H_6^+$ coincides with a notable increase in relative intensity of $Ta_2O_{4-5}(C_6H_6)_2^+$ at ~0.35 mTorr for $Ta_2O_{4-5}^+$. Therefore, it seems that $Ta_xO_yC_6H_6^+$ is undergoing further reactions at higher pressures, which is demonstrated in reaction 12. It is noted that the relative intensity of the $Ta_2O_5C_4H_4^+$ reaction channel in Figure 8b does increase to some extent at pressures above 0.35 mTorr, but it is thought that this product contributes only slightly to the uncharacteristic branching ratio behavior. The $Ta_2O_5(C_6H_6)_2^+$ reaction channel exhibits quite a dramatic rise in relative intensity, which is for the most part the factor that contributes to the uncharacteristic branching ratio behavior. Possibly, this uncharacteristic branching ratio behavior was observed for only $Ta_2O_{4-5}^+$ with benzene because the $Ta_2O_{4-5}C_6H_6^+$ product is still reactive for these particular clusters, but not for the other clusters studied.

$$Ta_xO_yC_6H_6^+ + C_6H_6 \rightarrow Ta_xO_y(C_6H_6)_2^+ \qquad (12)$$

Table 1 shows that the main reaction pathway of tantalum oxide cluster cations with 1-butene and 1,3-butadiene is cleavage of C−C bonds. The major product is cleavage of the α C−C bond of both 1-butene and 1,3-butadiene to form the $Ta_xO_yC_2H_4^+$ reaction channel. This is most likely the major product because it is thermodynamically favorable to break the α C−C bond of 1-butene and 1,3-butadiene. There were also additional cracking products, $Ta_xO_yCH_3^+$ and $Ta_xO_yC_3H_z$+ where $z = 5-6$, for reactions of tantalum oxide clusters with 1-butene and 1,3-butadiene. Cleavage of these C−C bonds over the C2−C3 bond is not thermodynamically favored, and it is postulated that these reaction products occur due to the strong metal−ligand bonds that third row transition metals form, thereby making them highly reactive species.[22] This idea is developed more completely later in the discussion. Table 1 also shows that the reactions of tantalum oxide cluster cations with 1-butene and 1,3-butadiene are not selective in the sense that most of the bonds of the hydrocarbon can be activated by tantalum oxide cluster cations, resulting in a broad distribution of reaction products.

Figures 1−6 show differences in the reactivity of tantalum oxide clusters with 1-butene and 1,3-butadiene. It is evident upon contrasting these figures that $Ta_2O_4^+$ and TaO_2^+ are the most reactive clusters toward cleavage of the α C−C bonds of both 1-butene and 1,3-butadiene to form the $Ta_xO_yC_2H_4^+$ reaction channel. Upon examination of Figures 1−6, it is apparent that the clusters TaO_3^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ are not as reactive as TaO_2^+ and $Ta_2O_4^+$ toward cracking 1-butene and 1,3-butadiene. This is most likely due to factors such as size, stoichiometry, and degree of coordinative saturation. Previously it has been reported that TaO_2^+, $Ta_2O_4^+$, $Ta_3O_7^+$, and $Ta_4O_9^+$ are the first peaks in their respective series in the total ion mass distribution of tantalum oxide cluster cations.[21] It is postulated that the reactions of tantalum oxide clusters with these unsaturated hydrocarbons are metal-mediated reactions, where the cluster cation interacts with the electron-rich unsaturated hydrocarbon. The stoichiometry of TaO_2^+ and $Ta_2O_4^+$, which is more metal-rich than the other tantalum oxide clusters in the total ion mass distribution, may be the reason that these clusters are the most reactive toward cracking 1-butene and 1,3-butadiene. Conversely, TaO_3^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ possess a more oxygen-rich stoichiometry than TaO_2^+ and $Ta_2O_4^+$ and therefore may not as reactive toward cleaving the C−C bonds of 1-butene and 1,3-butadiene. Additionally, it has been determined that C−C bond activation requires a high degree of coordinative unsaturation.[23] Therefore, another factor to consider is that TaO_2^+ and $Ta_2O_4^+$ are less coordinatively saturated than the other clusters investigated in this study, which may also contribute to their increased reactivity toward cracking 1-butene and 1,3-butadiene. On the contrary, TaO_3^+, $Ta_2O_4^+$, and $Ta_3O_7^+$ are more coordinatively saturated than TaO_2^+ and $Ta_2O_4^+$, which could cause a decrease in the reactivity of these particular clusters toward cleaving the C−C bonds of 1-butene and 1,3-butadiene.

Wise et al. revealed that Ta^+ has an extraordinary degree of reactivity toward dehydrogenating alkanes and alkenes.[24,25] In fact, Ta^+ was found to be one of the few gas-phase cations that has the ability to activate the C−H bonds of methane. Therefore, part of the focus of our studies was on reactions of tantalum oxide clusters with deuterated 1,3-butadiene to determine if dehydrogenation occurs. Through these studies with deuterated 1,3-butadiene it was determined that the clusters TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ form $Ta_xO_yC_2D_2^+$ and $Ta_xO_yC_2D_4^+$ reaction channels. Additionally, in the case of TaO_2^+ and $Ta_2O_4^+$, dehydrogenation of deuterated 1,3-butadiene occurs to give the $Ta_xO_yC_4D_4^+$ product which is not observed for any other clusters studied. These particular clusters may be especially reactive toward the dehydrogenation of deuterated 1,3-butadiene because of the lower degree of coordinative saturation and the more metal-rich stoichiometry compared to other clusters studied.

Reactions of vanadium oxide cluster cations with 1-butene and 1,3-butadiene also have been studied in our laboratory.[9] Since vanadium and tantalum are both group V transition metals, one might expect similar reaction products, but there are noticeable differences upon comparing the reaction products of vanadium and tantalum oxide clusters with 1-butene and 1,3-butadiene. For example, under multiple collision conditions TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ exhibit secondary reaction products, which are defined as $Ta_xO_yC_5H_z^+$ and $Ta_xO_yC_6H_z^+$ where $z = 7-10$, but vanadium oxide clusters do not exhibit these same reaction channels.

One of the reasons that tantalum oxide clusters display these secondary reaction products might be due to oligomerization of the hydrocarbon. Beauchamp and co-workers have found that the oligomerization of methane by Ta^+ is observed to give the products of up to $Ta(CH_2)_4^+$,[26] but these oligomerization reactions are not observed in the reactions of V^+ methane. Additionally, in the condensed phase tantalum complexes have been used to catalyze the polymerization of ethylene[27] and 2-butyne.[28] Unfortunately, our current experimental apparatus cannot be used to determine the structures of the reaction products on the clusters and therefore cannot be employed to ascertain whether oligomerization is occurring in these particular reactions.

Another possible reason that might explain why tantalum oxide clusters exhibit secondary reaction products could be that the cluster undergoes further reactions at higher pressures, where separate metal−carbon bonds are formed. Tantalum has an atomic radius of 1.34 Å, while the atomic radius of the vanadium atom is 1.22 Å.[29] Therefore, tantalum oxides could exhibit secondary reaction products because the tantalum oxide clusters are larger than the vanadium oxide clusters, which would allow more ligands to attach to the cluster. In fact, it has been found that the larger sizes of the elements of the third row transition series compared to those of the first row lead to a general tendency of the third row transition metals to exhibit higher coordination numbers than first row transition metals.[30,31] This has been illustrated clearly in the total ion mass distributions of tantalum[21] and vanadium[9] oxide cations by the fact that tantalum oxide clusters can accommodate more oxygen ligands than the vanadium oxide clusters. The final clusters in each series for tantalum are approximately TaO_{10}^+, $Ta_2O_{14}^+$, $Ta_3O_{14}^+$, and $Ta_4O_{14}^+$ [21] and the final clusters in each series for vanadium are approximately VO_5^+, $V_2O_8^+$, $V_3O_9^+$, and $V_4O_{12}^+$.[9] Therefore, it is apparent that tantalum oxide clusters can accommodate more ligands than vanadium oxide clusters with the same number of metal atoms, which is another possible explanation as to why secondary reaction products were formed for tantalum oxide clusters and not for vanadium oxide clusters.

Another difference between reactions of vanadium and tantalum oxide clusters with 1-butene and 1,3-butadiene is that tantalum oxide clusters exhibit cracking products of $Ta_xO_yCH_3^+$ and $Ta_xO_yC_3H_z^+$, where $z = 5-6$, as shown in reactions 2, 3, 6, and 7. These products were not observed in reactions of vanadium oxide clusters with 1-butene and 1,3-butadiene.[9] In order for a reaction to proceed favorably, the bonds formed during the reaction must be stronger than the bonds broken during the reaction. Therefore, the strength of the metal−ligand bonds should be taken into account when discussing the differences in reaction products of tantalum and vanadium oxide clusters with 1-butene and 1,3-butadiene.

It has been determined through theoretical generalized valence bond (GVB) calculations that metal−ligand bonds formed between third row transition metals are ordinarily stronger than those formed between first row transition metals.[22] This has been attributed to the lanthanide contraction, which leads to the tightening of the s orbitals of the third row transition metals between the elements lanthanum and hafnium.[32] Therefore, the lanthanide contraction in the 5d transition metals results in 6s and 5d orbitals that are very similar in size, which leads to optimum hybridization of s and d orbitals and strong metal−ligand bonds for third row transition metals.[33] Because of these stronger metal−ligand bonds there is a larger reaction exothermicity, which may explain the presence of $Ta_xO_yCH_3^+$ and $Ta_xO_yC_3H_z^+$ products, where $z = 5-6$, in reactions of tantalum oxide cluster cations with 1,3-butadiene and 1-butene. Conversely, hybridization of the s and d orbitals is more difficult for the first row transition metals because the relative size of the d orbital for the first row transition metals is small compared to the size of the valence s orbital, which leads to weaker metal−ligand bonds.[34] This may explain the absence of $V_xO_yCH_3^+$ and $V_xO_yC_3H_z^+$ products, where $z = 5-6$, in reactions of vanadium oxide clusters with 1-butene and 1,3-butadiene. As stated previously, it is believed that the reactions of the metal oxide clusters occur at metal centers, which will interact with the electron-rich hydrocarbon. Therefore, the fact that most Ta−ligand bonds are stronger than V−ligand bonds is quite significant in terms of what reaction products are formed in reactions of tantalum and vanadium oxide cluster cations with 1-butene and 1,3-butadiene.

Another striking difference between the reactions of vanadium and tantalum oxide cluster cations is that the major product in reactions of vanadium oxide cluster cations with 1,3-butadiene is dehydration,[9] which is demonstrated in reaction 13. However,

$$V_xO_y^+ + C_4H_6 \rightarrow V_xO_{y-1}C_4H_4^+ + H_2O \qquad (13)$$

the main reaction product of tantalum oxide cluster cations with 1,3-butadiene is C2−C3 cracking, which is shown in reaction 5, without formation of this dehydration product in reaction 13. The differences in the reaction products of tantalum and vanadium oxide cluster cations with 1,3-butadiene also may be explained by comparing metal−ligand bond strengths. In order for dehydration of 1,3-butadiene with vanadium oxide cluster cations to occur, at least one V^+−O bond needs to be cleaved. Dehydration is not observed in reactions of tantalum oxide clusters with 1,3-butadiene. Following the trends discussed previously, the strength of the V^+−O bond was determined to be 138 kcal/mol,[36] whereas the strength of the Ta^+−O bond was found to be 189 kcal/mol.[37] It is understood that the M^+−O bond strength in the vanadium and tantalum oxide clusters will not be the same as the bond strength values stated above because the bond strength changes depending on how many metal and oxygen atoms are present in a cluster. For example the value of the OV^+−O bond is 70.6 kcal/mol,[38] which is about 67 kcal/mol weaker than the V^+−O bond. However, it is highly probable that Ta^+−O bonds are generally stronger than the stoichiometrically equivalent V^+−O bonds in these metal oxide clusters. Therefore, it is possible that vanadium oxide clusters could exhibit a dehydration product with 1,3-butadiene, where at least one V^+−O bond would be broken, and tantalum oxide clusters do not exhibit this product due to stronger Ta^+−O bonds.

The reactions of tantalum oxide clusters with benzene were also studied as part of the present investigation. Benzene is relatively inert to fragmentation reactions compared to other alkenes because of the additional resonance stability of 36 kcal/mol.[35] Thermal reactions of the bare tantalum monomer cation with benzene have been probed by various investigators, and both dehydrogenation and ring cleavage products were formed.[24,25,36,37] Other transition metal monomer cations react with benzene to produce only the benzene association channel, $M^+(C_6H_6)$, or the benzene dehydrogenation channels, $M^+(C_6H_x)$, where $x = 2$ or 4.[38] Cleavage of the benzene ring reveals the highly reactive nature of Ta^+ because this is a high energy process, which involves both the loss of aromaticity and C−C bond breaking. In the case of tantalum oxide clusters, there are two major reaction products, which are dehydration, shown in reaction 9, and cleavage of the stable benzene ring, shown in reaction 8. Figures 7−9 reveal the differences in reactivity of tantalum oxide clusters due to size, stoichiometry, and degree of coordinative unsaturation of the particular cluster. All of the clusters displayed association of benzene onto the tantalum oxide cluster, but this is where the similarities in reactivity of the clusters cease. One of the most apparent observations is the lack of reactivity of TaO_3^+ and $Ta_3O_7^+$ with benzene as shown in Figures 7b and 9a. The benzene association channels are very strong for both of these clusters; however, there are not any other reaction products present except a minor dehydration channel for TaO_3^+ at high pressures. $Ta_3O_7^+$ shows a greater uptake of benzene compared to TaO_3^+, which is perhaps due to more metal sites of $Ta_3O_7^+$ compared to that of TaO_3^+. It seems odd that TaO_3^+ and $Ta_3O_7^+$ are unreactive toward benzene because both of these clusters are reactive toward both 1-butene and 1,3-butadiene, as previously mentioned. According to Zakin et al., the difference in the reactivities of different niobium clusters toward benzene may be due to the character of the cluster surface valence orbitals.[39] It is possible that the structures of TaO_3^+ and $Ta_3O_7^+$ are such that benzene LUMOs have poor spatial overlap with the cluster HOMOs of the appropriate energy and symmetry,[40] which could give rise to increased activation barriers for the cracking and dehydration reactions that occurred on other tantalum oxide clusters. Therefore it is possible that TaO_3^+ and $Ta_3O_7^+$ are not reactive with benzene, as they are with linear unsaturated hydrocarbons, because the orbitals of these clusters do not overlap appropriately with the benzene orbitals in order for reactions to proceed. Conversely, it is possible that cracking and dehydration channels were observed during reactions of TaO_2^+, $Ta_2O_{4-5}^+$, and $Ta_3O_8^+$ with benzene because the cluster orbitals and the benzene orbitals overlap appropriately, which enables these reactions to facilely proceed.

The major product of the reactions of $Ta_2O_{4-5}^+$ and $Ta_3O_8^+$ is the cracking product, $Ta_xO_yC_4H_4^+$. Interestingly, $Ta_3O_8^+$ is reactive toward cleavage of the benzene ring, yet this cluster only showed association products when reacted with 1-butene and 1,3-butadiene. Upon comparison of Figures 7−9, it is clear that $Ta_3O_8^+$ is the most reactive cluster toward cracking the benzene ring. There is also an additional cracking channel, $Ta_3O_7C_4H_2^+$, in the reactions of $Ta_3O_8^+$ with benzene, which is not observed for any other clusters. The increased propensity of $Ta_3O_8^+$ toward cracking benzene may be due to the size of this cluster compared to the smaller clusters examined. On most metal surfaces the benzene ring chemisorbs with the molecular ring parallel to the surface,[41] which would require a minimal number of interaction sites. El-Sayed and co-workers have suggested that a minimum number of niobium cluster−benzene bonds are required to properly anchor the benzene, which will drive the chemical reaction and destroy the chemical stability of benzene.[42] Since $Ta_3O_8^+$ is larger than the other clusters studied, there may be more interaction sites for the π-electrons of the benzene on $Ta_3O_8^+$ compared to the smaller clusters and more cluster−benzene bonds can be formed, which could aid in driving the cracking reactions of this cluster compared to the smaller clusters. The major product for TaO_2^+, and a minor product for $Ta_2O_{4-5}^+$ and $Ta_3O_8^+$ in reactions with benzene, is dehydration as shown in reaction 9. Perhaps since TaO_2^+ is the smallest cluster studied, there is less interaction of the cluster with the benzene ring compared to the larger clusters and for this reason ring cleavage is not the major reaction product.

The major reaction channel of oxygen-rich tantalum oxide clusters, $TaO_{y\geq 4}^+$, $Ta_2O_{y\geq 6}^+$, and $Ta_3O_{y\geq 9}^+$, is molecular oxygen loss to form stoichiometric clusters during reactions with the unsaturated hydrocarbons. This molecular oxygen loss channel is most likely due to a collision-induced dissociation (CID) process because these clusters exhibited loss of O_2 during CID experiments at thermal energies.[21] It was proposed that these oxygen-rich clusters are stoichiometric clusters with a chemisorbed O_2 molecule. All the stoichiometric fragments of the oxygen-rich clusters studied exhibited association of the hydrocarbon onto the stoichiometric fragment. The stoichiometric fragments of TaO_4^+, $Ta_2O_6^+$, and $Ta_3O_{10}^+$ exhibited additional reaction channels with the hydrocarbons studied. When TaO_4^+ reacted with 1-butene, 1,3-butadiene, and benzene, a TaO_2^+ fragment was produced, which exhibited C−C cracking reaction channels. When $Ta_3O_{10}^+$ was reacted with benzene, a $Ta_3O_8^+$ fragment was produced, which further reacted to form a benzene cracking channel. Lastly, when $Ta_2O_6^+$ was reacted with 1-butene and benzene, a $Ta_2O_5^+$ fragment was formed, which further reacted with these gases.

Conclusion

The reactivities of tantalum oxide cluster ions were investigated using a triple quadrupole mass spectrometer. The branching ratios of stoichiometric tantalum oxide clusters (TaO_{2-3}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_{7-8}^+$) with 1-butene, 1,3-butadiene, and benzene are reported and demonstrate the difference in the reactivities of these clusters toward the aforementioned hydrocarbons. The C2−C3 cracking product of TaO_2^+ and $Ta_2O_4^+$ displayed an uncharacteristic branching ratio behavior for their reactions with 1-butene and 1,3-butadiene. Similarly, the benzene association product of $Ta_2O_4^+$ and $Ta_2O_5^+$ displayed an uncharacteristic branching ratio behavior in the branching ratio during reactions with benzene. It was determined that this uncharacteristic branching ratio behavior is not pressure dependent. However, it was concluded that this phenomenon could be due to the formation of secondary reaction products at higher pressures. The reactions of tantalum oxide clusters with 1-butene and 1,3-butadiene were compared to the reactions of vanadium oxides with the same hydrocarbons. Upon comparison of the reactions of vanadium and tantalum oxides, it appears that tantalum oxide clusters are more reactive toward cracking the hydrocarbon than vanadium oxide clusters and that different reaction products are formed. It seems that tantalum oxides are more reactive than vanadium oxides because in general the metal−ligand bond strength is greater for 5d transition metals, which results in third row transition metals that are more reactive than their lighter congeners. Even though tantalum oxide clusters are quite reactive toward cracking 1-butene and 1,3-butadiene, these reactions are not selective in terms of which bonds are broken or the stoichiometry of the tantalum oxide cluster. It was also determined by experiments with deuterated 1,3-butadiene that dehydrogenation of the hydrocarbon occurs in reactions with certain tantalum oxide cluster cations. Reactions of tantalum oxide clusters with benzene displayed cracking of the stable benzene ring, which attests to the highly reactive nature of these tantalum oxide cluster cations. The major reaction channels of the oxygen-rich tantalum oxide clusters are loss of O_2 to form the stoichiometric clusters, which then proceed to react with or associate the hydrocarbon gas.

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