Reactivities of tantalum oxide cluster cations with unsaturated hydrocarbons

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Abstract

The reactivities of tantalum oxide cluster cations with unsaturated hydrocarbons have been probed using a triple quadrupole mass spectrometer coupled with a laser vaporization source. The reaction pathways observed for the tantalum oxide clusters with 1,3-butadiene (C_4H_6), 1-butene (C_4H_8), and (D6)benzene (C_6D_6) include association, atomic and molecular oxygen loss, cracking, minor dehydration, and possible dehydrogenation with the reactivities of different clusters varying from species to species. In the case of 1,3-butadiene, the major reaction product involves cracking of the C2–C3 bond to give $Ta_xO_y^+(C_2H_4)$ reaction channels. The major reaction of tantalum oxide clusters with 1-butene is again cracking of the C2–C3 bond to give $Ta_xO_y^+(C_2H_4)$ reaction products. Lastly, cracking of the stable benzene ring to give $Ta_xO_y^+(C_4D_4)$ is the major reaction pathway for tantalum oxide clusters interacting with (D6) benzene. (Int J Mass Spectrom 184 (1999) 119–128) © 1999 Elsevier Science B.V.

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1. Introduction

Group V transition metal oxides are important to the field of catalysis. There are numerous industrial processes that are either catalyzed by vanadium or niobium oxides or that use vanadium or niobium oxides as supports for catalysts because of their highly reducible nature [1]. For example, vanadium oxides have been used to catalyze the selective oxidation of *o*-xylene to produce phthalic anhydride [2] and for the ammoxidation of toluene into benzonitrile [3]. Niobium oxides have been used as promoters on a V_2O_5/TiO_2 catalyst for the decomposition of nitric oxide [4] and as supports for palladium and cobalt catalysts for the synthesis of tetrahydrofuran [5]. Additionally, niobic acid ($Nb_2O_5 \cdot nH_2O$) has been used to catalyze the hydration of ethylene to ethyl alcohol [6]. Reactions catalyzed by vanadium and niobium oxides have been extensively studied and characterized, but the catalytic properties of tantalum oxides are seldom examined. Tantalum oxides have been shown to successfully catalyze vapor phase Beckmann rearrangements [7] and hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) catalyzes the esterification of methacrylic acid [8]. Even though Group V transition metal oxide catalysts are used frequently in industrial processes, a complete understanding of the relation-

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ship between the local structure of metal oxides and the catalytic behavior of the oxide has not yet been established.

There are numerous reasons for studying catalytic behavior using gas-phase metal oxide clusters. First, the surface composition of a metal oxide is different from that of the bulk phase. The surface consists of numerous dangling bonds and therefore has many coordinatively unsaturated sites. For this reason, the oxidation state and stoichiometry vary across the entire surface of a metal oxide. By studying transition metal oxides in the gas phase, we can select different oxidation states, stoichiometries, and charges in order to determine what effects these factors have on catalytic behavior, which is difficult to achieve using typical surface spectroscopy techniques. Furthermore, mechanisms of reactions progressing over metal oxide catalysts in the bulk are obscured by irregular structure and adsorption [9], but by using gas-phase studies these difficulties are avoided. Additionally, the surface structure of bulk transition metal oxides can be viewed as an assemblage of clusters of different sizes and isomers. Finally, clusters can be considered the simplest model of the interaction of active sites on an oxide catalyst with organic molecules. For these reasons, gas-phase studies of Group V metal oxide clusters can assist in understanding the nature of the reactive sites on heterogeneous catalysts.

There have been various studies on the reactivities of bare transition metal cations (M^+) and monomeric metal oxide cations (MO^+) with hydrocarbons in the gas phase [10,11], mostly in the area of activation of the C–C or C–H bonds of saturated hydrocarbons. However, there have been limited studies on reactivities of transition metal oxide clusters. Zamaraev and co-workers have shown that there are indeed similarities between interactions of methanol with molybdenum oxide cations in the gas phase and reactions of methanol over real molybdenum/oxygen catalysts [12]. Deng et al. have reported the collision induced dissociation (CID) and reactivities of a small number of niobium oxide cluster cations with 1,3-butadiene, acetone, and benzene [13]. Recently, Bell et al. have extensively studied the reactivities of vanadium oxide clusters with industrially important gases such as

n-butane, 1-butene, and 1,3-butadiene along with the CID of vanadium oxide clusters [14]. The compelling reason to study tantalum oxide cluster cations is because they have not been very well studied and characterized in the bulk phase and not much is known about their potential catalytic activity.

2. Experimental

The instrument used to study the reactivities of tantalum oxide clusters is a triple quadrupole mass spectrometer system coupled with a laser vaporization source, which has been described previously [15,16]. Briefly, the second harmonic output of a Nd:YAG laser (5–20 mJ/pulse, 20 Hz) is focused onto a metal rod, which is translated and rotated so that each pulse of the laser beam ablates a fresh metal surface. A pulse valve is used to introduce pulses of a mixture of oxygen seeded in helium ($\sim$10%) over the ablated rod, where plasma reactions take place and metal oxide clusters are produced. The clusters are cooled by supersonic expansion as they exit the source into the first differentially pumped region of the instrument. The cluster beam is collimated as it passes through a 3 mm skimmer and into the first set of electrostatic lenses. These are used to guide and focus the ion beam into the first quadrupole. The first quadrupole is where the ion of interest, $Ta_xO_y^+$, is selected from the entire cluster distribution of tantalum oxide cations. 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 either as a reaction cell or a collision cell. A capacitance manometer (MKS) is used to monitor the pressure of the gas in the second quadrupole. After the collisions or reactions occur, the product ions exit the second quadrupole into a third set of electrostatic lenses and then enter the third quadrupole where the products are mass analyzed and finally detected by a channeltron electron multiplier. The signal goes through a preamplifier-discriminator and is stored with a personal computer via a multichannel scalar card.
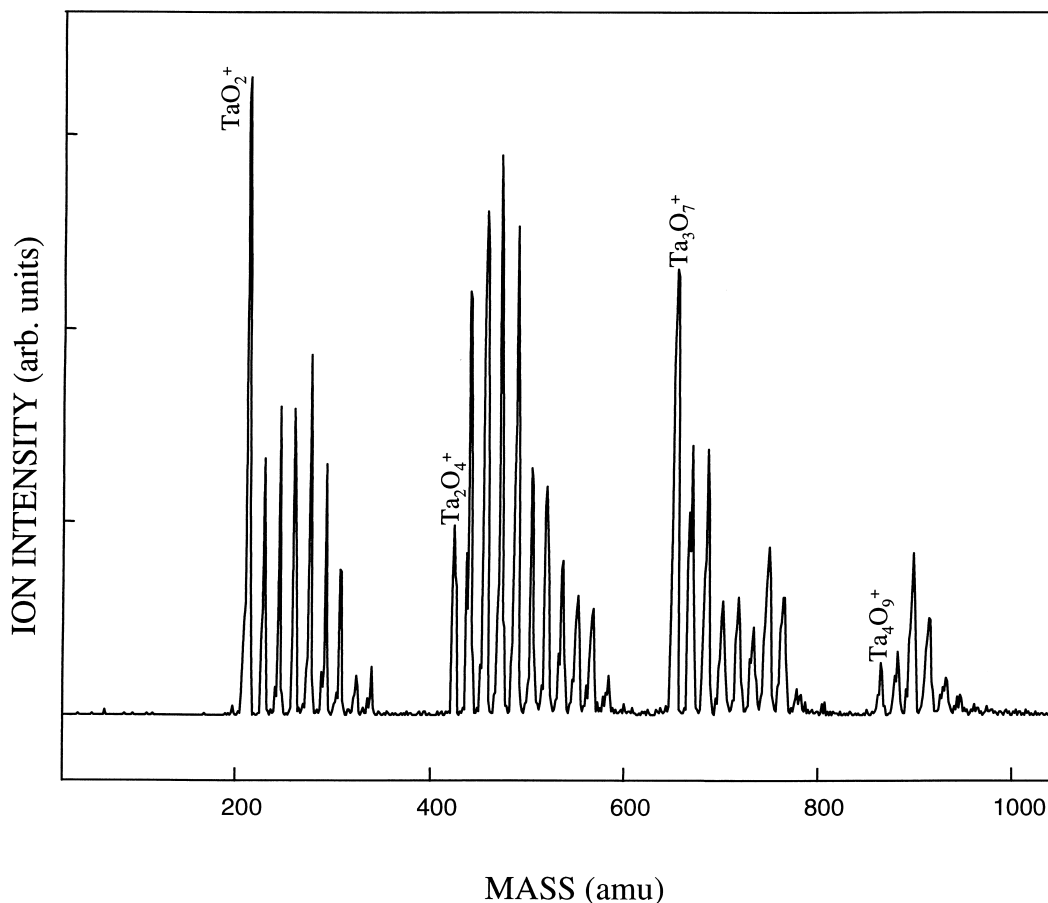
Fig. 1. Total ion mass distribution of tantalum oxide cluster cations.

3. Results

Currently, tantalum oxide cation reactivities have been probed in our laboratory using unsaturated gases, such as 1,3-butadiene, 1-butene, and (D6)benzene. These reactivity studies were performed at pressures of reactant gas ranging from 0.15–0.25 mTorr, which correspond to multiple collision conditions in our system. 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. The reaction pathways of the tantalum oxide clusters with these hydrocarbon gases include: association,

oxygen transfer, cracking, minor dehydration, and possible dehydrogenation.

The tantalum oxide cluster mass distribution is shown in Fig. 1. Considering the mass distribution, it is clear that there are various reaction centers with different oxidation states and stoichiometries that we can select to study. It can also be seen from the mass distribution that the first peak in each series is of the building block $(TaO_2)_m(Ta_2O_5)_n$, where $m = 1–2$ and $n = 0–1$. This stoichiometry corresponds to the bulk phase stoichiometry of tantalum oxides, which is TaO_2 and Ta_2O_5 [17]. The reactivities of only eight of the $Ta_xO_y^+$ clusters (TaO_{1-2}^+, $Ta_2O_{4-6}^+$, $Ta_3O_{7-9}^+$) produced in the mass distribution are reported here.

Collision induced dissociation results are shown in

Table 1
Collision induced dissociation results of tantalum oxide clusters[a]

Tantalum oxide cluster	CID products
TaO_2^+	...
TaO_3^+	...
TaO_4^+	TaO_2^+
TaO_5^+	TaO_3^+
$Ta_2O_4^+$	...
$Ta_2O_5^+$	...
$Ta_2O_6^+$	$Ta_2O_4^+$
$Ta_2O_7^+$	$Ta_2O_5^+$
$Ta_3O_7^+$	...
$Ta_3O_8^+$	...
$Ta_3O_9^+$	$Ta_3O_7^+$
$Ta_3O_{10}^+$	$Ta_3O_8^+$

[a] At single collision conditions and near thermal energies.

Table 1. These results indicate that $TaO_{y\geq4}^+$, $Ta_2O_{y\geq6}^+$, and $Ta_3O_{y\geq9}^+$ are oxygen rich clusters. That is, when krypton gas is added at single collision conditions into the collision cell, the aforementioned clusters lose O_2 at thermal energies. It is postulated that the O_2 is weakly bound onto the surface of the stoichiometric clusters. For example, the $Ta_2O_6^+$ cluster is simply $Ta_2O_4^+$ with an O_2 molecule chemisorbed onto the surface. This is further evidenced by the reactions of the oxygen rich tantalum oxide clusters with the unsaturated hydrocarbons. The oxygen rich clusters will lose O_2 to form the stoichiometric cluster, which will proceed to react with the hydrocarbon gas. For example, $Ta_3O_9^+$ will lose O_2 to form $Ta_3O_7^+$ and this species may undergo a reaction with the hydrocarbon gas, but its oxygen rich precursor will not.
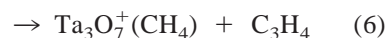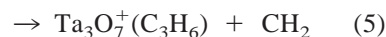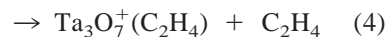
3.1. Reactivity with 1,3-butadiene

Fig. 2 shows the reaction of $Ta_3O_7^+$ with 1,3-butadiene and Table 2 summarizes the reactions of the other tantalum oxide clusters with 1,3-butadiene. All of the $Ta_xO_y^+$ clusters studied, with the exception of $Ta_2O_6^+$ and $Ta_3O_9^+$, formed molecular association products with 1,3-butadiene to give the $Ta_xO_y^+(C_4H_6)$ adduct. Most of the clusters studied, except $Ta_2O_6^+$ and $Ta_3O_{8-9}^+$, cracked the C2–C3 bond of 1,3-butadiene to give reaction channel of $Ta_xO_y^+(C_2H_4)$. The proposed reaction scheme of $Ta_3O_7^+$ with 1,3-butadiene can be described as:

$$Ta_3O_7^+ \ + \ C_4H_6 \rightarrow Ta_3O_7^+(C_4H_6) \qquad (1)$$

$$\rightarrow Ta_3O_7^+(C_2H_4) \ + \ C_2H_2 \qquad (2)$$
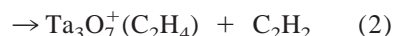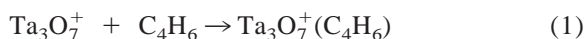
Interestingly, the neutral product of the cracking of 1,3-butadiene is acetylene, which is an industrially important hydrocarbon. $Ta_2O_4^+$ is the most reactive cluster studied toward cracking the C2–C3 bond of 1,3-butadiene. The cluster $Ta_2O_5^+$ can be considered nonselective because in addition to cracking the 1,3-butadiene, a minor dehydration channel was observed. The oxygen rich clusters, which are $Ta_2O_6^+$ and $Ta_3O_9^+$ both lose molecular oxygen to form $Ta_xO_{y-2}^+$ when reacted with 1,3-butadiene. Additionally, $Ta_2O_6^+$ exhibited a single oxygen loss channel to form $Ta_2O_5^+$.

3.2. Reactivity with 1-butene

Fig. 3 shows the reaction of $Ta_3O_7^+$ with 1-butene and Table 2 gives a summary of the reactions of the other clusters studied with 1-butene. All of the $Ta_xO_y^+$ clusters studied, with the exception of $Ta_2O_6^+$ and $Ta_3O_9^+$, formed molecular association products with 1-butene to give $Ta_xO_y^+(C_4H_8)$ addition channels. Apparently, TaO_{1-2}^+ both singly dehydrogenates and doubly dehydrogenates 1-butene to give $TaO_{1-2}^+(C_4H_6)$ and $TaO_{1-2}^+(C_4H_4)$. However, more extensive studies need to be performed to study the possible dehydrogenation channels by using deuterated 1-butene. TaO_{1-2}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ all exhibited a major cracking channel of $Ta_xO_y^+(C_2H_4)$ and two minor cracking channels of $Ta_xO_y^+(C_3H_6)$ and $Ta_xO_y^+(CH_4)$. The proposed reaction scheme of $Ta_3O_7^+$ with 1-butene can be described as follows:

$$Ta_3O_7^+ \ + \ C_4H_8 \ \rightarrow \ Ta_3O_7^+(C_4H_8) \qquad (3)$$

$$\rightarrow \ Ta_3O_7^+(C_2H_4) \ + \ C_2H_4 \qquad (4)$$

$$\rightarrow \ Ta_3O_7^+(C_3H_6) \ + \ CH_2 \qquad (5)$$

$$\rightarrow \ Ta_3O_7^+(CH_4) \ + \ C_3H_4 \qquad (6)$$

TaO_2^+ and $Ta_2O_4^+$ were the most reactive in cracking 1-butene. Similar to the reactions with 1,3-butadiene, $Ta_3O_9^+$ exhibited loss of molecular oxygen. $Ta_2O_{5-6}^+$
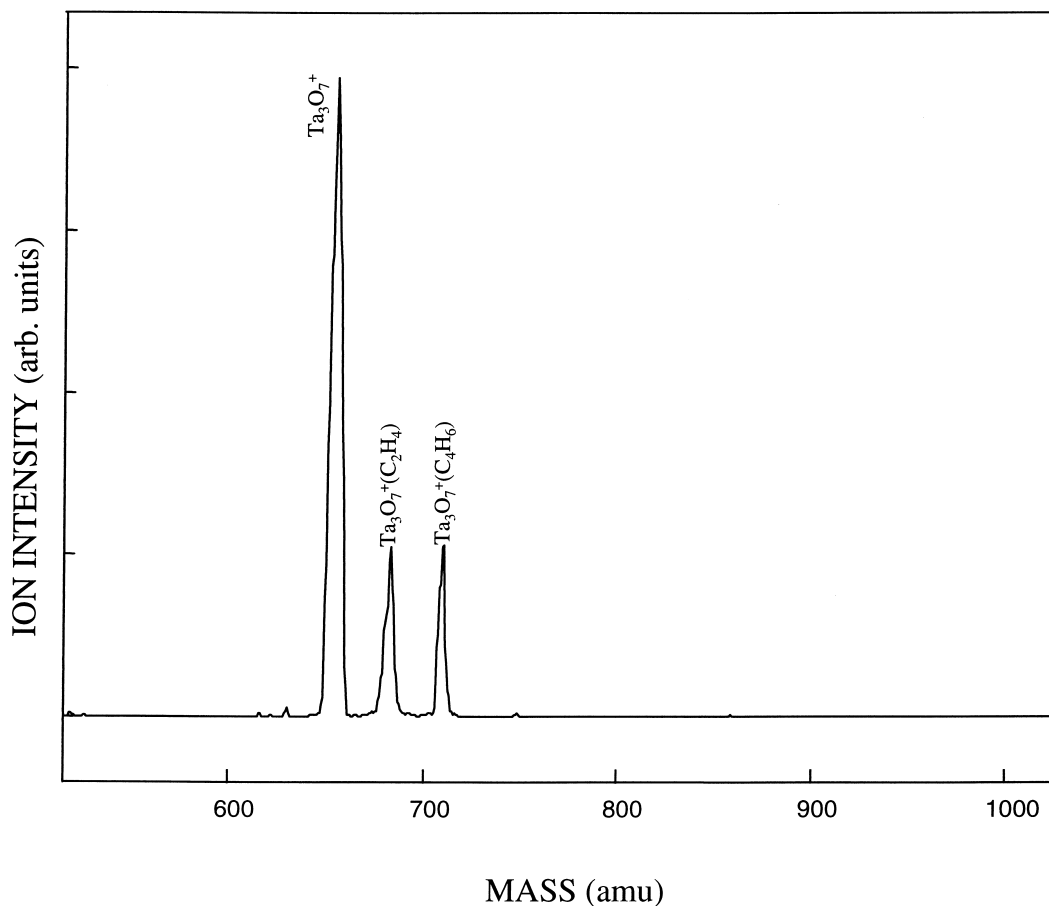
Fig. 2. Spectrum of the reaction of $Ta_3O_7^+$ with 0.19 mTorr 1,3-butadiene near thermal energies. This reaction displays C2–C3 cracking of 1,3-butadiene, which forms the product $Ta_3O_7^+(C_2H_4)$.

are unique because they both show a single oxygen loss channel to form a $Ta_2O_{4-5}^+$ peak.

3.3. Reactivity with (D6)benzene

A spectrum of the reaction of $Ta_2O_5^+$ with (D6)-benzene is shown in Fig. 4. A summary of the reactions of the tantalum oxide clusters with (D6)-benzene is shown in Table 2. All of the $Ta_xO_y^+$ clusters studied, except $Ta_3O_9^+$, produced molecular association products with (D6)benzene to give the $Ta_xO_y^+(C_6D_6)$ association channel. TaO_2^+, $Ta_2O_{4-6}^+$, and $Ta_3O_8^+$ cracked the stable aromatic ring of (D6)benzene to give reaction channels of

$Ta_xO_y^+(C_4D_4)$. The proposed reaction scheme of $Ta_2O_5^+$ with (D6)benzene can be described as:

$$Ta_2O_5^+ \ + \ C_6D_6 \ \rightarrow \ Ta_2O_5^+(C_6D_6) \qquad (7)$$

$$\rightarrow \ Ta_2O_5^+(C_4D_4) \ + \ C_2D_2 \quad (8)$$
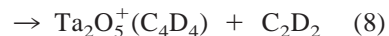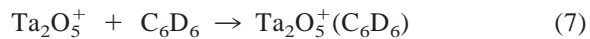
Cracking of benzene is a process which would have significant environmental benefits by converting highly toxic aromatics into industrially useful hydrocarbons. Cracking of the benzene ring was unexpected because benzene has additional resonance stability of 36 kcal/mol, which makes it relatively inert to fragmentation reactions [18]. $Ta_3O_8^+$ is the most reactive cluster studied toward cracking

Table 2
Summary of reactions of tantalum oxides with unsaturated hydrocarbons

$Ta_xO_y^+$	1,3-Butadiene	1-Butene	(D6)Benzene
TaO^+	$TaO^+(C_4H_6)$	$TaO^+(C_4H_6)^a$	
	$TaO^+(C_2H_4)$	$TaO^+(C_4H_4)^a$	
		$TaO^+(C_4H_8)$	
		$TaO^+(C_2H_4)$	
		$TaO^+(C_3H_6)$	
		$TaO^+(CH_4)$	
TaO_2^+	$TaO_2^+(C_4H_6)$	$TaO_2^+(C_4H_6)^a$	$TaO_2^+(C_6D_6)$
	$TaO_2^+(C_2H_4)$	$TaO_2^+(C_4H_4)^a$	$TaO^+(C_6D_4)$
		$TaO_2^+(C_4H_8)$	$TaO_2^+(C_4D_4)$
		$TaO_2^+(C_2H_4)$	
		$TaO_2^+(C_3H_6)$	
		$TaO_2^+(CH_4)$	
$Ta_2O_4^+$	$Ta_2O_4^+(C_2H_4)$	$Ta_2O_4^+(C_2H_4)$	$Ta_2O_4^+(C_6D_6)$
	$Ta_2O_4^+(C_4H_6)$	$Ta_2O_4^+(CH_4)$	$Ta_2O_4^+(C_4D_4)$
		$Ta_2O_4^+(C_3H_6)$	
		$Ta_2O_4^+(C_4H_8)$	
$Ta_2O_5^+$	$Ta_2O_5^+(C_2H_4)$	$Ta_2O_5^+(C_2H_4)$	$Ta_2O_5^+(C_6D_6)$
	$Ta_2O_5^+(C_4H_6)$	$Ta_2O_5^+(CH_4)$	$Ta_2O_5^+(C_4D_4)$
	$Ta_2O_4^+(C_4H_4)$	$Ta_2O_5^+(C_3H_6)$	$Ta_2O_4^+$
		$Ta_2O_5^+(C_4H_8)$	
		$Ta_2O_4^+$	
$Ta_2O_6^+$	$Ta_2O_5^+(C_2H_4)$	$Ta_2O_5^+$	$Ta_2O_6^+(C_6D_6)$
	$Ta_2O_5^+$	$Ta_2O_5^+(C_2H_4)$	$Ta_2O_6^+(C_4D_4)$
	$Ta_2O_4^+$	$Ta_2O_5^+(C_4H_8)$	$Ta_2O_5^+(C_6D_4)$
			$Ta_2O_5^+$
$Ta_3O_7^+$	$Ta_3O_7^+(C_4H_6)$	$Ta_3O_7^+(C_4H_8)$	$Ta_3O_7^+(C_6D_6)$
	$Ta_3O_7^+(C_2H_4)$	$Ta_3O_7^+(C_2H_4)$	
		$Ta_3O_7^+(C_3H_6)$	
		$Ta_3O_7^+(CH_4)$	
$Ta_3O_8^+$	$Ta_3O_8^+(C_4H_6)$	$Ta_3O_8^+(C_4H_8)$	$Ta_3O_8^+(C_6D_6)$
			$Ta_3O_8^+(C_4D_4)$
			$Ta_3O_7^+(C_6D_4)$
			$Ta_3O_7^+(C_4D_2)$
$Ta_3O_9^+$	$Ta_3O_7^+(C_4H_6)$	$Ta_3O_7^+(C_4H_8)$	$Ta_3O_7^+(C_6D_6)$
	$Ta_3O_7^+$	$Ta_3O_7^+$	$Ta_3O_7^+$

^a Indicates possible dehydrogenation product.

(D6)benzene, which is puzzling because the $Ta_3O_8^+$ cluster with 1,3-butadiene and 1-butene did not have a reaction channel. TaO_2^+ displayed a cracking channel, but the major reaction channel for this cluster is dehydration. The major reaction channels for the clusters $Ta_2O_6^+$ and $Ta_3O_8^+$ is cracking, but they also displayed a minor dehydration channel. $Ta_3O_9^+$ lost molecular oxygen when reacted with (D6)benzene. Additionally, $Ta_2O_{5-6}^+$ both exhibited a single oxygen loss channel to form $Ta_2O_{4-5}^+$.

4. Discussion

Many different reaction pathways have been reported for the reactions of unsaturated hydrocarbons with tantalum oxide clusters including: association, oxygen transfer, cracking, minor dehydration, and possible dehydrogenation. The loss of molecular oxygen from the oxygen rich clusters when reacted with unsaturated hydrocarbons is most likely because of a CID process. As reported earlier, these clusters exhibited loss of O_2 at single collision conditions and near thermal energies. Specifically, $Ta_3O_9^+$ with 1,3-butadiene, 1-butene, and (D6)benzene and $Ta_2O_6^+$ with 1,3-butadiene showed this molecular oxygen loss. However, $Ta_2O_6^+$ showed a single oxygen loss channel when reacted with all three of the unsaturated hydrocarbons studied and $Ta_2O_5^+$ showed an atomic oxygen loss channel when reacted with 1-butene. The CID results did not indicate a single oxygen loss product for any of the tantalum oxide clusters studied. Therefore, it is postulated that these reactions are because of oxygen transfer from the selected cluster ($Ta_2O_{5-6}^+$) to the unsaturated hydrocarbon to leave the single oxygen loss product ($Ta_2O_{4-5}^+$).

The major reaction products of both 1,3-butadiene and 1-butene with tantalum oxides were cracking of the α C–C bonds of the respective hydrocarbons to give the reaction channel of $Ta_xO_y^+(C_2H_4)$. This is most likely because of the favorability of cleaving this particular bond. The bond strength of a C–C bond is 88 kcal/mol, which is considerably lower than the C = C bond strength of 152 kcal/mol. Multiple cracking products, such as $Ta_xO_y^+(C_3H_6)$ and $Ta_xO_y^+(CH_4)$, are observed when the tantalum oxides are reacted with 1-butene. However, these reaction products are not detected when tantalum oxides are reacted with 1,3-butadiene. This may be because of the fact that 1-butene has one double bond, as compared to 1,3-butadiene that has two double bonds. Therefore cracking can also occur at the C3–C4 bond of 1-butene in addition to the C2–C3 bond. By contrast, reactions of 1,3-butadiene might only have enough energy to break the C2–C3 bond of the 1,3-butadiene.

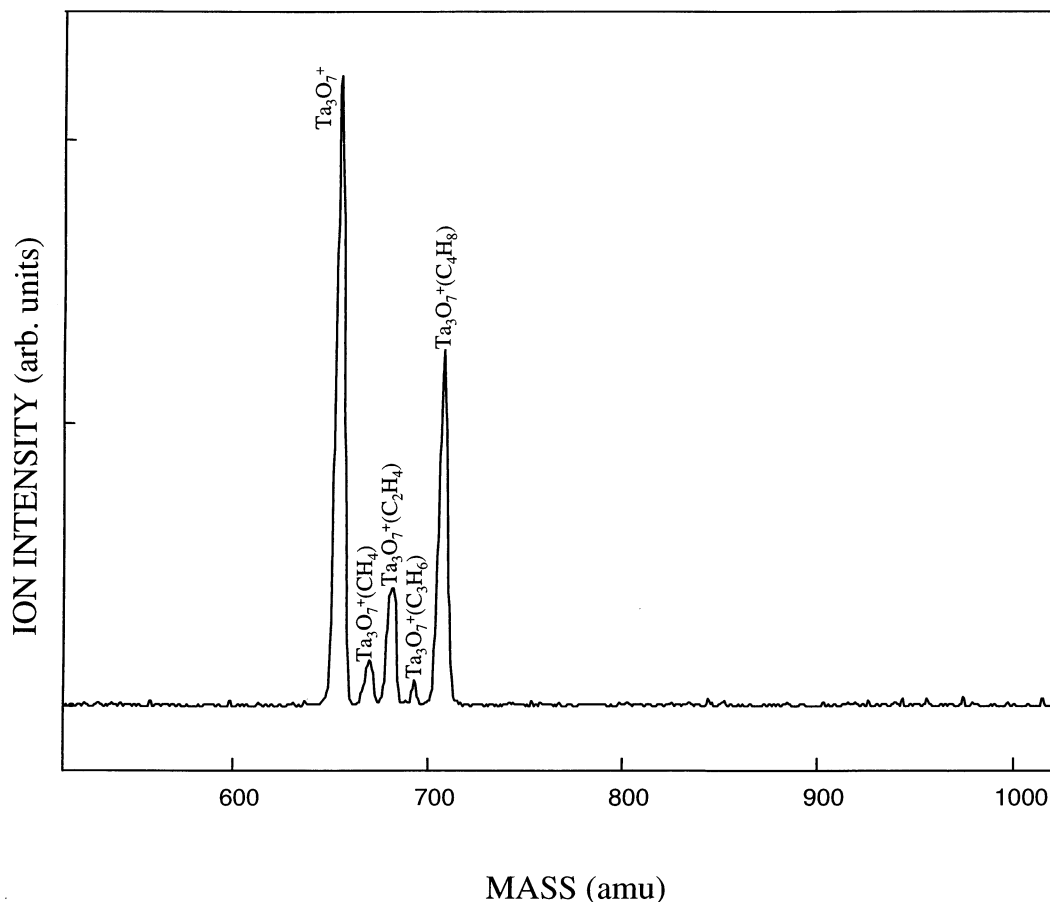The major reaction products of (D6)benzene with

Fig. 3. Spectrum of the reaction of $Ta_3O_7^+$ with 0.21 mTorr of 1-butene near thermal energies. This reaction displays C2–C3 cracking of 1-butene, which forms the product $Ta_3O_7^+(C_2H_4)$. Also minor cracking products of $Ta_3O_7^+(C_3H_6)$ and $Ta_3O_7^+(CH_4)$ are observed.

tantalum oxides is cracking of the stable benzene ring. The reactivities of certain clusters with (D6)benzene differ from the reactivities of these clusters with the linear unsaturated hydrocarbons that were studied. Cracking channels were observed for TaO_{1-2}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$ when reacted with 1,3-butadiene and 1-butene. $Ta_3O_8^+$ displayed only a minor simple addition peak. In contrast, the tantalum oxide clusters that exhibited cracking of the benzene ring were TaO_2^+, $Ta_2O_{4-6}^+$, and $Ta_3O_8^+$. $Ta_3O_7^+$ was unreactive and simply displayed a simple addition product. $Ta_3O_8^+$ was the most reactive toward reactions with benzene. Because the $Ta_3O_8^+$ cluster is larger than the other clusters studied, it may have more possible sites for interaction with the π electrons of

the benzene, which may make the cracking of the benzene ring more likely for the larger cluster as compared to the smaller clusters studied. However, $Ta_3O_8^+$ just simply added the linear unsaturated gases studied. The differences in the cluster reactivities with different unsaturated hydrocarbons may be because of the way the aromatic ring interacts with the cluster in contrast to the way the linear unsaturated hydrocarbons interact with the clusters. Further experiments and calculations need to be performed to explain the differences in reactivities with these unsaturated hydrocarbons.

Bell et al. determined that there is a size dependence on the reactivities of vanadium oxide clusters with 1-butene and 1,3-butadiene [14]. It was found
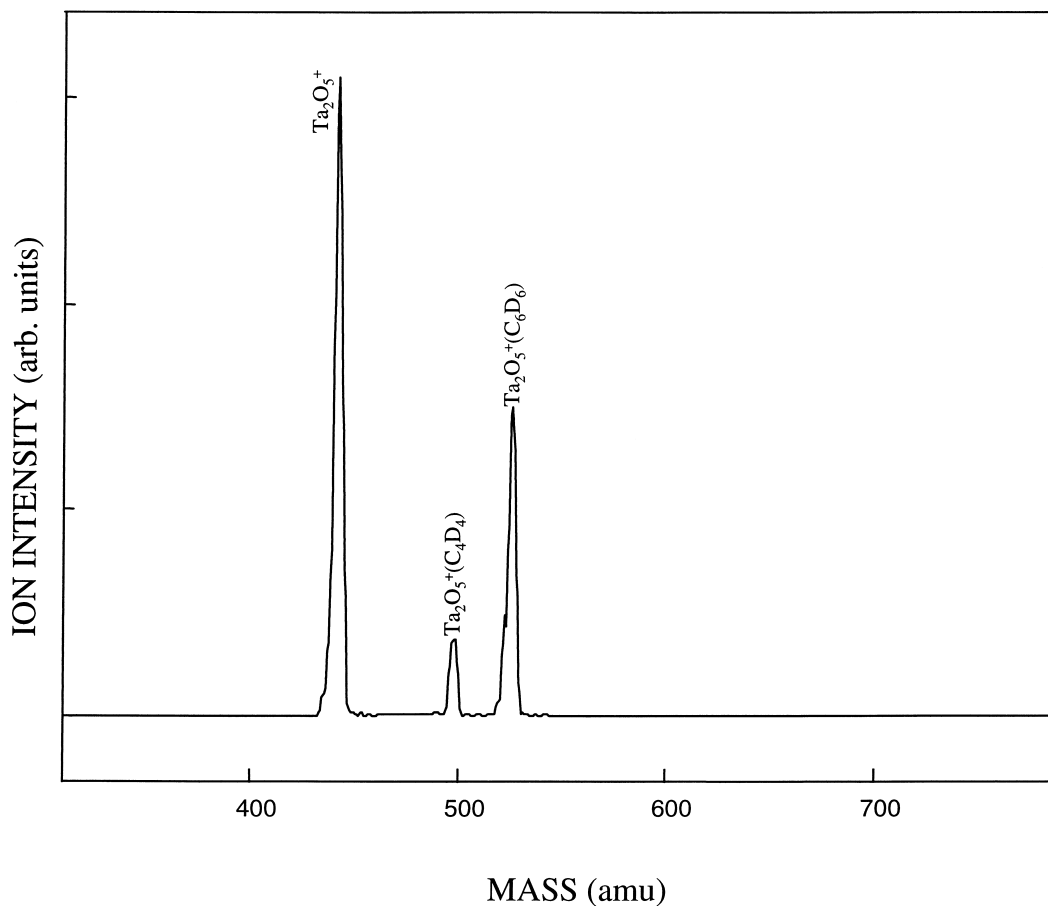
Fig. 4. Spectrum of the reaction of $Ta_2O_5^+$ with 0.15 mTorr of (D6)benzene near thermal conditions. This reaction shows cracking of (D6)benzene that forms the product $Ta_2O_5^+(C_4D_4)$.

that as the size of the cluster increased, the reactivity of the cluster decreased. For example, $V_3O_7^+$ was very reactive toward dehydrating 1,3-butadiene, but $V_5O_{12}^+$ was much less reactive toward dehydrating 1,3-butadiene. Current studies on tantalum oxides at pressures ranging from 0.15–0.25 mTorr suggest the same general trend in their reactivities as those of vanadium. It was discovered that the most reactive tantalum oxide clusters toward 1,3-butadiene and 1-butene were TaO_2^+ and $Ta_2O_4^+$. In contrast, the reactions of the tantalum oxide clusters with (D6)benzene have an opposite trend of size dependence. The larger the size of the cluster, the more reactive the cluster is toward cracking the benzene ring. For example, $Ta_3O_8^+$ was very reactive toward cracking of (D6)benzene and

TaO_2^+ was much less reactive toward cracking (D6)benzene. These findings exclude the possibility that the trends in reactivity depend on the energy content of the clusters.

Another reaction channel that was observed in these reactions of tantalum oxides with 1,3-butadiene and (D6)benzene was dehydration. $Ta_2O_5^+$ showed a minor dehydration channel when reacted with 1,3-butadiene. TaO_2^+, $Ta_2O_6^+$, and $Ta_3O_8^+$ also displayed dehydration channels when reacted with (D6)benzene. TaO_2^+ had a dehydration channel that is more significant than the cracking channel for this particular reaction. The final reaction channel that was possibly observed was single and double dehydrogenation of 1-butene by TaO_{1-2}^+. However,

reactions of deuterated 1-butene with tantalum oxide clusters need to be performed in order to conclude if dehydrogenation of 1-butene is indeed occurring.

As mentioned previously, reactivity studies have been performed using both vanadium and niobium oxides. Currently, the only common reactant gas that has been studied with all of the Group V transition metal oxides is 1,3-butadiene. In the case of niobium, only $Nb_3O_{7-8}^+$ clusters were studied and there were no reaction products, just simple addition of 1,3-butadiene [13]. The reactivities of the vanadium oxides were thoroughly studied with both 1,3-butadiene and 1-butene [14]. $V_2O_4^+$, $V_3O_7^+$, and $V_5O_{12}^+$ all exhibited a dehydration channel upon reacting with 1,3-butadiene. $V_2O_4^+$ also showed a minor cracking product. By contrast, the major reactant channel in the tantalum oxides is the cracking of the C2–C3 bond of 1,3-butadiene, which was observed in TaO_{1-2}^+, $Ta_2O_{4-5}^+$, and $Ta_3O_7^+$. Both the vanadium oxides and the tantalum oxides were studied with 1-butene. The major reaction channels for both the vanadium and tantalum oxides were cracking of the C2–C3 bond of 1-butene. The tantalum oxides also exhibited two additional minor cracking channels of $Ta_xO_y^+(C_3H_6)$ and $Ta_xO_y^+(CH_4)$. The extent of cracking of the C2–C3 bond of 1-butene with tantalum oxides was generally much greater than the cracking of the hydrocarbon using the vanadium oxides. Last, niobium and tantalum oxides were both studied with benzene. When $Nb_3O_7^+$ was reacted with benzene, there were no reaction products, just an addition channel [13]. This is in great contrast to the tantalum oxides that, when reacted with benzene, showed extensive cracking of the stable benzene ring. From the results reported herein, it seems the tantalum oxides have a high affinity toward cracking unsaturated hydrocarbons.

5. Conclusion

From the limited amount of experiments that have been performed, the reactivities of the Group V transition metal oxides seem to differ greatly. How-ever, more experiments need to be done to establish a larger base of comparison of the reactivities of the Group V transition metal oxides with hydrocarbons. Collision induced dissociation experiments of stoichiometric tantalum oxide clusters need to be performed at elevated energies. These experiments along with *ab initio* calculations will help in better understanding these reactions, in postulating mechanisms, and to propose structures of the tantalum oxide clusters. Also the deuterated species of 1-butene need to be studied in order to determine if dehydrogenation is occurring. More extensive work needs to be performed with aromatic hydrocarbons. Studies of other aromatic hydrocarbons need to be performed to gain insight into why $Ta_3O_8^+$ is so reactive toward benzene, but unreactive with linear unsaturated hydrocarbons. Finally, further studies are required to aid in explaining why tantalum oxides are so reactive toward cracking unsaturated hydrocarbons and to explain the differences in the reactivities of the clusters.

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