



Size-dependent gas phase reactivity of tantalum cluster cations with small alcohols



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ABSTRACT

Small tantalum cluster cations (Ta_{4-9}^+) were produced in the gas phase by laser vaporization. Various alcohols (methanol, ethanol, *n*-propanol and 2-propanol) were consecutively added to the cluster beam in a pulsed jet and allowed to react to an extent of conversion of approximately 50%. The charged reaction products were subsequently measured using time of flight mass spectrometry. Two distinct reaction pathways were observed, involving complete dehydrogenation or OH abstraction from the alcohol molecule. The relative total reaction yield was found to not vary significantly within the cluster size regime studied. The branching ratios for the reaction demonstrated a cluster-size dependence, with a minimum of OH abstraction occurring for Ta_7^+ .

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1. Introduction

In recent decades it has been shown that typically non-reactive bulk metal species can be reactive for particle sizes in the non-scalable (cluster) size regime [1]. Furthermore, it has been discovered that the reactivity within this regime depends on particle size, can vary on a per atom basis [2–6], and can be isomer sensitive [7]. The study of gas phase reactions of metal clusters and metal containing systems has been shown to provide important information on reaction mechanics and remains a highly topical field [8–10]. While the application of nanoparticulate metal catalysts in industrial scale reactions is already well advanced, even smaller, size-selected clusters have been touted as potentially more efficient replacements [11]. Some examples of industrially important reactions are the activation and subsequent conversion of alkanes as well as the conversion of methanol to formaldehyde. Small tantalum and tantalum oxide clusters have been shown to activate alkanes [12,13] and theoretical studies show that the dehydrogenation of methanol by the atomic cation is energetically favorable [14].

In comparison to the precious metals often used as catalysts, tantalum is relatively inexpensive and abundant. It is then surprising that relatively few reactivity studies of small tantalum clusters have been performed. One of the few works in this field was performed by Cao et al. [14], who studied the gas phase reactions of the atomic Nb, V and Ta cations with methanol using Fourier Transform Ion Cyclotron Resonance mass spectrometry (FT-ICR). The reaction products found to be in common for reactions with all three metals were the formation of MO^+ and MOH^+ . For the atomic cations of Nb and V, $M(CH_3O)^+$ and $M(CH_2O)^+$ were also formed. While the dehydrogenation reaction was not observed in the case of Ta^+ , viz., $Ta(CH_3OH)^+ \rightarrow Ta(CH_2O)^+ + H_2$, it was calculated to be energetically favorable with an overall energy change of -78.5 kcal/mol [14]. Similar reaction products have also been found for the reaction of small alcohols with other metal and metal oxide cations [15,16].

The dehydrogenation reaction pathway was observed in the reaction of gas phase neutral tantalum clusters with unsaturated hydrocarbons by He et al. [17]. The unsaturated hydrocarbons were added via a pickup cell and the neutral reaction products were measured using laser ionization mass spectrometry. It was found that completely dehydrogenated association products for clusters larger than the trimer (e.g. Ta_nC_6 for the reaction of neutral tantalum clusters with benzene, where $n > 3$) were highly favored, with partial dehydrogenation products only observed in special cases.

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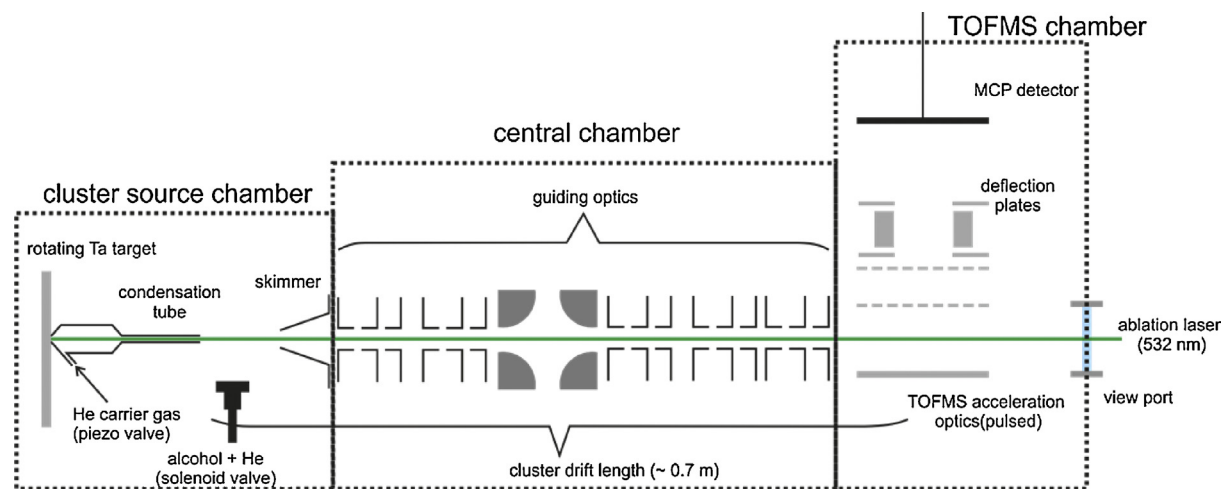


Fig. 1. Schematic of the experimental setup. Clusters are formed in a laser vaporization source and expanded into vacuum by a He gas pulse. Immediately after this expansion, alcohol molecules are introduced into the vacuum through a pulsed valve. The positively charged cluster and cluster-adsorbate species are then guided by numerous Einzel lenses to a TOFMS. Here, the ions are extracted perpendicularly by a high voltage pulse and detected with a microchannel plate detector (note that the quadrupole bender functions as a linear ion guide for this experiment).

Furthermore, reaction products resulting from the interaction of the Ta clusters with multiple hydrocarbon molecules were found in the form of carbon chain building and metcar (M_8C_{12}) formation.

The reactions of tantalum oxide clusters have been studied more thoroughly and in one such study Zemski et al. investigated the reactions of a number of small hydrocarbons with tantalum oxide cluster cations and anions in the gas phase [18–20]. The primary reaction mechanisms were identified as C–C insertion of the metal oxides, leading to carbon chain cracking.

Insights about the reactivity of niobium and niobium oxide clusters provide useful direction to studies involving tantalum clusters. Jackson et al. [21] exposed niobium oxide cluster anions to alcohol molecules in an FT-ICR mass spectrometer. The most important recurring mechanism was the initial attachment of the alcohol at a metal-oxygen double bond. The major reaction pathways were found to involve hydroxyl abstraction and alkyl fragment liberation, association and dehydration and, finally, oxidation. Dehydrogenation was only found to occur in special cases.

In this work we report the size-dependent reactivity of tantalum cluster cations with alcohol molecules in the gas phase. The results for cationic tantalum clusters Ta_n ($n = 4–9$) with several alcohols are shown and the size dependency of the observed reaction products is discussed.

2. Experimental

The experimental setup used in this study is described for the first time here and is accompanied by a schematic, which is shown in Fig. 1. Metal clusters were produced in a metal disc type laser vaporization cluster source that is similar to the source reported previously by Heiz et al. [22]. Vaporization of the metal target was performed with the second harmonic of a Nd:YAG laser (Innolas Spitlight DPSS), timed to coincide with a pulse of helium carrier gas (Westfalen AG, Helium 6.0). The cluster source condensation tube has a length of 60 mm and a diameter of 2 mm.

The alcohols were introduced into the vacuum in the cluster source chamber immediately after the cluster expansion using a pulsed solenoid valve (General valve, series 9) resulting in an average pressure of 1×10^{-2} mbar in the chamber. A stainless steel vessel was filled with the alcohol of interest and helium backing gas (Westfalen AG, Helium 5.0) was bubbled through the liquid alcohol. The general valve was pulsed and timed to coincide with the expansion of the cluster beam from the cluster source using a

delay generator (Stanford Research Systems, DG645). The cluster and alcohol beams were crossed perpendicularly within the source chamber.

Following skimming of the entrained metal cluster-alcohol beam, the nascent cationic species were guided to the time of flight mass spectrometer (TOFMS) using a number of Einzel lenses. The time of flight mass spectrometer utilized a homebuilt Wiley McLaren, two stage design and consists of annular plates constructed from stainless steel. The plates have an inner diameter of 40 mm, which are covered with mesh wherever changes in the electric field strengths occur. Deflection plates were mounted directly after the TOFMS electrodes and were used to steer the ion beam to the detector. The electrodes of the TOFMS were pulsed to high voltage using a pair of power supplies (FuG Elektronik GmbH, HCP 14-6500) connected to two high voltage pulsing units (homebuilt with HV switches from Behlke Power Electronics GmbH, ± 6.5 kV) at the arrival time of the ions. The ions were then extracted orthogonally into the 300 mm long drift region of the linear TOFMS. The ions were subsequently detected with a microchannel plate detector (Photonic, APD 2 MA 40/12/10/8 D60:1, chevron configuration). Spectra were visualized and recorded using an oscilloscope (LeCroy Waverunner, 44Xi-A). The mass resolution of the experimental setup was measured to be approximately 250. The presented spectra were created by averaging 1000 individual traces.

3. Results

Typical mass spectra of the reaction products of cationic tantalum clusters Ta_n ($n = 4–9$) with methanol, ethanol, *n*-propanol and 2-propanol are shown in Fig. 2. The major peaks in the spectra correspond to the bare metal clusters, but numerous reacted species are also observed. The major reaction product peaks are located at the parent metal cluster mass plus 17 and 28, 40 or 52 μ , depending upon the parent alcohol and are assigned to OH and dehydrogenated alcohols attached to the metal clusters, respectively. Example reaction schemes are given in Eqs. (1) and (2) below. The small peaks at masses larger than the reactant alcohol-cluster association mass were assigned to co-adsorbed products such as $(C_xO)(OH)$ originating from the reaction of one cluster with more than one alcohol molecule. Given the aforementioned low intensities, the 1:2 and higher cluster:alcohol stoichiometric products are not considered further in this work. The structural composition of the reaction products are as of yet unknown, though previous

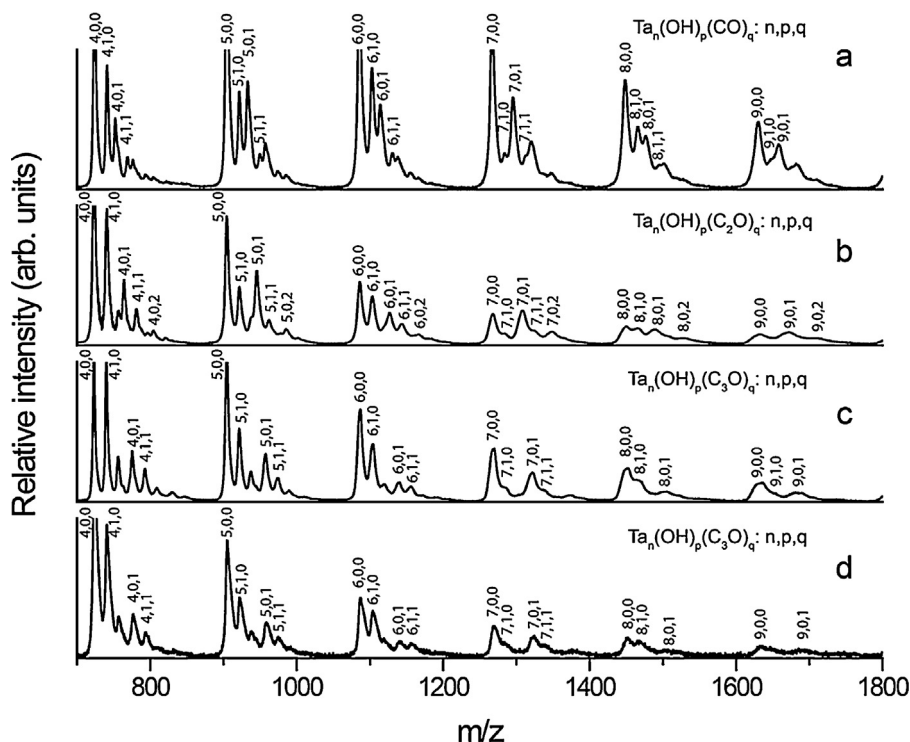
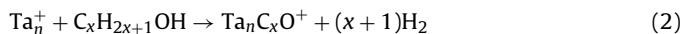
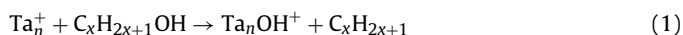


Fig. 2. Mass spectra of nascent tantalum cations reacted with: (a) methanol, (b) ethanol, (c) *n*-propanol and (d) 2-propanol. The major reaction products are assigned to Ta_nOH^+ and $Ta_nC_xO^+$ and a cluster size dependent intensity of the reaction products is observed. The highest intensity Ta_n^+ peaks have been truncated to ensure better viewing of the reaction product signal (see Fig. S1 in the supporting information for the non-truncated spectra).

calculations indicate that the dehydrogenated product does not dissociate completely and is bound to the metal through the oxygen atom [14].



The branching ratios of the metal-hydroxide products for Ta_{4-9}^+ were calculated from the relative intensity of the respective peaks relating to the two major reaction pathways (i.e. by division by the sum of both reaction products), and are recorded in Table S1 located in the supporting information. The branching ratios only reflect the case of the single cluster-molecule collision stoichiometry and do not consider any association-dissociation pathways. The latter would have resulted in bare metal cluster cations and therefore cannot be discriminated from unreacted metal cluster cations. No data from secondary reactions have been included in the calculation of the branching ratios. It is assumed that quantification of these data at the current extent of reaction would result in little (1–3%) to no change of the reported branching ratios. The ratios were plotted versus cluster size and are presented in Fig. 3.

To exclude the possibility that the alcohol molecules are affected by the laser vaporization process, ethanol was seeded directly into the cluster backing gas in a further experiment. The resulting spectrum shown in Fig. S2 in the supporting information features many product peaks that correspond to the formation of carbides e.g. $Ta_nC_x^+$, $n=1-6$, $x=1-6$. Minor peaks corresponding to Ta_nOH^+ (in competition with Ta_nO^+) and $Ta_nC_2O^+$ are also observed, but at lower intensities than the carbide species.

A measure of the total reactivity of the tantalum clusters is presented in Fig. S3 in the supporting information. Here the intensities of the 1:1 stoichiometry reaction products are summed and compared to the total intensity of the signals for each cluster size. It can be seen from the plot that the overall reactivity of the tantalum cluster cations does not change considerably with cluster size. All

four experiments reported here were performed at similar extents of conversion to ensure the comparability of the results.

4. Discussion

As seeding of the carrier gas primarily leads to metal carbide formation, the formation of Ta_nOH^+ and $Ta_nC_xO^+$ is exclusively attributed to the reaction of Ta_n^+ with the respective alcohol molecule. The two reaction products are therefore assigned to two different reaction pathways, which have previously been assigned

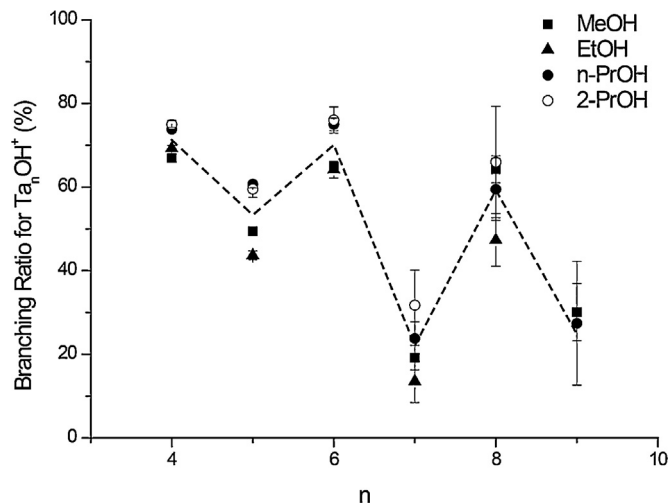


Fig. 3. Ta_nOH^+ product branching ratios resulting from the reaction of Ta_n^+ ($n=4-9$) with small alcohols. The dashed line represents the average values and is plotted to guide the eye. A clear size effect is found with a minimum of the hydroxide formation for Ta_7^+ . The error bars represent absolute errors that were calculated using Gaussian error propagation.

in the literature as initial C–O insertion and O–H insertion, respectively [14].

The time between reaction and measurement of the reaction products was fixed at approximately 1 ms. Given that no intact alcohol molecules can be detected on the clusters, 1 ms thus serves as an upper limit for the reaction time.

The observation of completely dehydrogenated products in the present study is the first time that such reaction products have been measured for the reaction of tantalum cationic clusters with alcohols. Despite being calculated to be energetically favorable, dehydrogenation of methanol following O–H insertion by Ta⁺ was not observed in the study of Cao et al. [14]. It was however observed for gas phase reactions of methanol with Nb⁺ and V⁺ [14].

Dehydrogenation reaction products have previously been identified for the gas phase reactions of neutral tantalum clusters with unsaturated hydrocarbons [17]. He et al. reported that the lack of collisional stabilization of the association products meant that the reactions proceeded to completion. Despite the presence of inert carrier gas atoms in both reactant expansions in the current work, it is unlikely that any considerable collisional cooling of the reaction intermediates or products takes place. The observation of completely dehydrogenated alcohols attached to the tantalum clusters is therefore in good agreement with the work of He et al. and the calculations performed by Cao et al.

From the branching ratios presented in Fig. 3 it is clear that the relative reaction product intensities are cluster size dependent. Cationic tantalum clusters with an odd number of atoms show an increased tendency for the formation of the dehydrogenation product (Ta_nC_xO⁺) relative to the cluster cations with an even number of atoms. The reaction products TaOH⁺ and Ta(CH₂O)⁺ were previously assigned to the initial insertion of Ta⁺ into the C–O and O–H bonds of methanol, respectively [14]. This implies that the reaction selectivity for Ta_n⁺ (*n* = 4–9) clusters with alcohol molecules observed in this study originates from the initial insertion of the clusters into the molecule. Previous theoretical studies of neutral tantalum clusters found the lowest energy geometries were very similar to those of Nb_n, with a transition to 3D structures at Ta₄ [26]. Experimental and theoretical studies of Ta_{6–8}⁺ [27] revealed structures similar to those found for the neutrals, but these structures cannot serve as a geometric link to the observed odd–even oscillation of the branching ratio. Instead, these odd–even oscillations can be assigned to the changing electronic parity of the tantalum clusters. Atomic tantalum has 73 electrons in the electronic configuration [Xe] 4f¹⁴ 5d³ 6s² and therefore clusters with even numbers of Ta atoms have at least one unpaired electron in their ionic form.

A global minimum for abstraction of OH from Ta_n⁺ (*n* = 4–9) is observed at Ta₇⁺. The Ta₇⁺ cluster has been previously assigned as a ‘magic number’ cluster [28] and has a highly symmetric structure (D_{5h}) with triplet spin multiplicity [27]. The inactivity of this cluster for the OH abstraction pathway may be related to its electronic stability.

From previous studies performed with a source based on the same design [23], as well as other, similar sources [24,25], it is assumed that the cluster temperatures are between 100 and 300 K. The collisional (kinetic) nature of the cooling in such laser vaporization sources implies that the internal temperatures of the clusters would not show an odd–even cluster size dependence, but would increase gradually with cluster size.

Unlike in the study of Cao et al. [14], TaO⁺ formation from the reaction of the atomic tantalum cation with alcohols was not observed with the current experimental setup. The reaction pathway that leads to the formation of TaO⁺ was assigned to be the low energy pathway following C–O insertion by Ta⁺ and requires the migration of the hydrogen from OH before reductively eliminating CH₄ [14]. TaOH⁺ formation was reported to occur via a high

energy pathway that is dominated by simple bond cleavage. This is supported by the work of Engeser et al., who reported branching ratios of the production of VO⁺ and VOH⁺ from the reaction of V⁺ with methanol that differed considerably from the results of Cao et al. [15]. These differences were assigned to the application of an efficient thermalization step prior to reaction in the work of Engeser et al., which lead to the preferential formation of VO⁺ [15].

While no production of TaO⁺ from reactions with alcohols was observed in this work, it is possible that the oxide signals for the larger cluster sizes are obscured by the large Ta_nOH⁺ signals, due to the mass resolution of the time of flight mass spectrometer. No obvious broadening of the tantalum hydroxide peaks toward lower masses is observed however, so it is assumed that possible Ta_nO⁺ signals are negligible.

5. Conclusion

Two major reaction pathways were found for the reaction of cationic tantalum clusters with alcohols in the gas phase. Association and total dehydrogenation of the alcohols was observed and was compared to previous gas phase reactivity studies of cationic tantalum clusters. A second pathway involving the abstraction and association of OH from the alcohols was identified and found to compete with the dehydrogenation reaction. The favored reaction pathway was determined to depend upon cluster size, with a minimum for the OH abstraction reaction observed at Ta₇⁺.

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