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Gas-Phase Chemistry of Vanadium Oxide Cluster Cations $V_mO_n^+$ (m = 1–4; n = 1–10) with Water and Molecular Oxygen

Sandra Feyel,[a] **Detlef Schröder,**[b] **and Helmut Schwarz***[a]

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Bare vanadium oxide cluster cations $V_mO_n^+$ (m = 1–4; n = 1–10) generated by electrospray ionization are investigated with respect to their reactivity toward water and molecular oxygen by using mass spectrometric techniques. Besides ion hydration, the ion/molecule reactions of $V_mO_n^+$ with oxygen-labeled water ($H_2{}^{18}O$) also lead to $^{16}O/^{18}O$ exchange reactions of the vanadium oxide clusters cations. Although the probability of degenerate $^{16}O/^{18}O$ exchange between $V_mO_n^+$ and water is fairly high for the cluster cations with a medium valence state of vanadium, oxygen-atom exchange reactions between $V_mO_n^+$ and $^{18}O_2$ can only be accomplished by VO^+, $V_3O_6^+$, and $V_4O_8^+$. Particularly interesting is the fact that not only oxygen atoms from vanadyl units are exchanged in the cluster cations, but bridging oxygen atoms are also most likely involved in the processes. Other reaction channels for the interaction of $V_mO_n^+$ cluster cations with molecular oxygen are reported as well, such as oxidative degradation of the low-valent cluster cations upon collision with O_2 and formation of association complexes for the high-valent cluster cations.

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Introduction

Vanadium oxides are among the most important transition-metal catalysts used in chemical technology,[1] for instance, in the production of SO_3 from SO_2, the conversion of propane to propene, or the large-scale synthesis of maleic anhydride from butane.[2] However, the mechanistic details of oxidation reactions occurring on vanadium oxide surfaces are far from being fully understood. For example, whereas it is quite likely that oxygen vacancies are present on the surfaces of vanadia catalysts, their precise catalytic function in the active site remains to be elucidated.[3]

In this context, a number of gaseous vanadium oxide clusters have been studied theoretically[4–6] as well as probed experimentally[7–15] with the aim to obtain information about structure/reactivity correlations, cluster-size effects, as well as the role of formal and real charges. Gas-phase studies can provide direct insight into the intrinsic properties of the clusters and moreover also may deepen the understanding of the reaction mechanisms by means of combining mass spectrometric experiments with labeling studies and theoretical approaches.[14,16]

In general, laser evaporation of the appropriate metal in the presence of oxygen is an excellent method to generate metal oxide cluster ions in the gas phase. However, the cluster structures formed in this way may not always be uniform. For example, tetravanadium decaoxide, $V_4O_{10}^+$, bears an isomeric dioxygen complex $V_4O_8(O_2)^+$, which is cogenerated upon laser evaporation.[11a,17] As an alternative means of cluster generation, electrospray ionization mass spectrometry (ESI-MS)[18] has opened up new horizons.[19,20] If appropriate precursors are employed, ESI can also provide access to vanadium oxide cluster cations of the type $V_mO_n^+$ (m = 1–4; n = 1–10).[15a,21] In order to provide direct evidence for the presence or absence of weakly bound dioxygen complexes, in this work we will explore the ion/molecule reactions (IMRs) of vanadium oxide cluster cations aimed at exchanging the putative O_2 ligand(s) toward water as well as $^{18}O_2$ used as probe molecules.[7,22]

Reactions with dioxygen are also relevant in the context of catalysis, because vanadium, as an early transition metal, is quite oxophilic and thus likely to form higher valence states in the presence of O_2. In turn, these high-valent vanadium compounds are required as the catalytically active sites relevant in various oxidation and oxygenation processes.[9h,15] In this context, oxygen isotopic exchange reactions occurring in the IMRs of $V_mO_n^+$ with O_2 are also a useful tool for characterizing oxygen conducting oxides.[23] In previous models put forward by Klier et al.[24] and Muzykantov et al.[25] three parallel processes were suggested to rationalize the $^{16}O/^{18}O$ exchange reactions of metal oxides: (1) The exchange proceeds without direct involvement of lattice oxygen, as the oxygen molecule exchanges one of its atoms with another oxygen molecule from the gas phase (R^0-mechanism):

$$^{18}O_2(g) + {}^{16}O_2(g) \rightarrow 2\ {}^{18}O^{16}O(g)$$

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[a] Institut für Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, 10623 Berlin, Germany
Fax +49-30-314-21102
E-mail: Helmut.Schwarz@mail.chem.tu-berlin.de
[b] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic,
Flemingovo nám. 2, 16610 Prague 6, Czech Republic

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(2) Only one O atom of O_2 is replaced by the surface oxygen of the metal oxide (R^1-mechanism):

$$^{18}O_2(g) + {}^{16}O(s) \rightarrow {}^{18}O^{16}O(g) + {}^{18}O(s)$$

(3) Both atoms of a single oxygen molecule are exchanged with the oxygen of the metal oxide (R^2-mechanism):

$$^{18}O_2(g) + 2\ {}^{16}O(s) \rightarrow {}^{16}O_2(g) + 2\ {}^{18}O(s)$$

Gas-phase reactions of the mass-selected metal oxide cluster ions will provide once more an important impulse in order to substantiate one or the other of the proposed mechanisms (R^0, R^1, and R^2) in terms of $^{16}O/^{18}O$ exchange reactions.

Results and Discussion

In the present work, ESI is used to generate mono-, di-, tri-, and tetranuclear vanadium oxide cluster cations as gas-phase species having the general formula $V_mO_n^+$ (m = 1–4; n = 1–10) and covering averaged, formal oxidation states of vanadium from 2.50 to 5.25. The generated vanadium oxide cluster cations are exposed to water and molecular oxygen in order to study their bimolecular reactivities to determine the nature of the interaction between the cationic clusters and the oxidant molecule as well as to study oxygen-atom exchange reactions.

IMRs of $V_mO_n^+$ with Water

As mentioned above, laser ablation of vanadium in the presence of dioxygen often leads to dioxygen complexes with the general formula $V_mO_{n-2}(O_2)^+$. Koyanagi et al. carried out IMRs of oxygen-rich mononuclear oxidovanadium peroxide cations with neutral water with the purpose to mediate exchange of the loosely bound dioxygen ligand(s) toward H_2O.[7] Accordingly, the structures of the generated $V_mO_n^+$ clusters can be probed in the IMR with water to determine whether peroxido ligands are present in the clusters and can be exchanged by a water molecule according to Equation (1). Moreover, the capabilities of the vanadium oxide clusters to activate water are indicated by the occurrence of isotopic exchange reactions with $H_2{}^{18}O$ according to Equation (2) as well; as will be shown pronounced cluster size effects exist.

$$V_mO_{n-2}(O_2)^+ + H_2O \rightarrow V_mO_{n-2}(H_2O)^+ + O_2 \qquad (1)$$

$$V_m{}^{16}O_n^+ + H_2{}^{18}O \rightarrow V_m{}^{16}O_{n-1}({}^{18}O)^+ + H_2{}^{16}O \qquad (2)$$

IMRs of mass-selected $V_mO_n^+$ were carried out with neutral water, and the mass differences and product-ion branching ratios are summarized in Table 1. Upon inspection of Table 1 it becomes clear that the IMRs of $V_mO_n^+$ clusters with light H_2O more or less lead to a single reaction channel, which corresponds to ligand association to form $V_mO_n(H_2O)^+$. The association reaction with water is not at all unexpected and preferred ion hydration has also been described by Koyanagi et al.[7] It is pointed out, however, that consecutive ion hydrations leading to larger hydrated clusters are not observed in our experiments carried out in a multipole mass spectrometer with a stationary pressure of water at around $p(H_2O) = 0.5 \times 10^{-4}$ mbar.[26]

Table 1. Mass differences (Δm given in amu), branching ratios (BR with $\Sigma BR_i = 100$), relative rate constants (k_{rel}), and formal valences of the vanadium atoms in the clusters (*f.v.*) in the IMRs of $V_mO_n^+$ cations with light and heavy water [$p(H_2O) = 0.5 \times 10^{-4}$ mbar; $p(H_2{}^{18}O) = 1.5 \times 10^{-4}$ mbar].

$V_mO_n^+$	*f.v.*	$\Delta m(H_2O)$ +18	k_{rel}[a]	$\Delta m(H_2{}^{18}O)$ + 2	$\Delta m(H_2{}^{18}O)$ + 20
VO^+	3.00	n.r.[b,c]			
VO_2^+	5.00	n.r.[c]	45	100	
$V_2O_2^+$	2.50	n.r.[c]			
$V_2O_3^+$	3.50	100[d]	15	10	80
$V_2O_4^+$	4.50	100	20	40	60
$V_3O_4^+$	3.00	100	40	55	45
$V_3O_5^+$	3.67	100	60	40	60
$V_3O_6^+$	4.33	100	100	20	80
$V_3O_7^+$	5.00	n.r.[c]			
$V_4O_7^+$	3.75	100	65	50	50
$V_4O_8^+$	4.25	100	60	40	60
$V_4O_9^+$	4.75	100	40	10	90
$V_4O_{10}^+$	5.25	n.r.[c]			

[a] The relative rate constants correspond to the IMR with $H_2{}^{18}O$. [b] Earlier experiments[7] already found the VO^+ cation to react quite inefficiently with water. [c] n.r. = no reaction, that is, the IMRs of VO_2^+, $V_3O_7^+$, and $V_4O_{10}^+$ did not result in any products above the noise level. [d] The IMRs of $V_2O_3^+$ with H_2O and $H_2{}^{18}O$ resulted also in a mass increase of $\Delta m = +16$, which is mainly ascribed to residual oxygen present in the background of the mass spectrometer; in the evaluation of the BRs this reaction channel is added to the BR obtained for adduct formation. Furthermore, IMR of $V_2O_3^+$ with $H_2{}^{18}O$ leads to a mass increase of $\Delta m = +18$, which is assigned to uptake of one oxygen atom concomitant with release of molecular hydrogen to form $V_2O_4^+$ (BR = 10%).

An exception is $V_2O_3^+$, as the IMR of this particular cluster ion with H_2O resulted also in a signal corresponding to a mass increase of $\Delta m = +16$ (BR = 50%; see Table 1, footnote d), which can be assigned to a net uptake of one oxygen atom. However, the labeling experiment of $V_2O_3^+$ with $H_2{}^{18}O$ (Table 1, footnote d) clearly indicates isobaric superposition for the latter signal: Due to separation by mass, the product ion can undoubtedly be assigned to uptake of an ^{18}O atom ($\Delta m = +18$) from water concomitant with elimination of H_2 as well as to exchange of a single light oxygen atom in the cluster cation toward an O_2 molecule (as verified below by experiments with $^{18}O_2$); the latter reactant is available in the background of the vacuum system. The ratio of the first and the latter product channel is found to be 1:8.

The absence of signals at $\Delta m = -14$ for all $V_mO_n^+$ species examined indicates that no exchange reaction of a loosely bound peroxido ligand toward a water molecule according to Equation (1) has taken place. This finding suggests that only oxygen atoms in vanadyl units, bridging oxygen atoms, or μ_2-peroxido ligands are present in the metal oxide cluster cations; weakly bound superoxido ligands can be excluded.

In addition to the hydration of the vanadium oxide cluster cations to produce $V_mO_n(H_2{}^{18}O)^+$ ($\Delta m = +20$), in the IMR with $H_2{}^{18}O$ a second set of signals is detected at Δm

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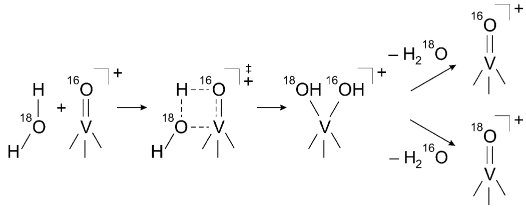
= +2, which is assigned to isotopic exchange of a light oxygen atom (^{16}O) in the cluster toward a heavy oxygen atom (^{18}O) [Table 1, Equation (2)].

Scheme 1 depicts a possible reaction mechanism for the oxygen-exchange reaction. With reference to theoretical work, we suggest the occurrence of a four-membered transition structure through which one hydrogen atom from the water molecule is transferred to a vanadyl unit concomitant with attachment of the labeled hydroxy group to the vanadium center, which thus leads to a metal dihydroxido unit.[7,27] Then, in a consecutive step, either light or heavy water is released to afford $V^{18}O$ and $V^{16}O$ moieties, respectively.



Scheme 1. Possible scenario for $^{16}O/^{18}O$ atom exchange occurring at a VO^+ unit in the reaction with $H_2{}^{18}O$.

The extent to which $^{16}O/^{18}O$ exchange with water takes place strongly depends on the size of the clusters and the degree of coordinative saturation with the oxido ligands. This becomes clear upon inspection of Figure 1 in which the relative rates of the oxygen-exchange reaction channel are plotted as a function of the formal valence of vanadium in the cluster cations. Obviously, only vanadium oxide cluster cations of medium valence states bring about $^{16}O/^{18}O$ exchange. It is also striking that the reaction rate for the vanadium oxide cluster cations capable of oxygen activation decreases very smoothly from mid-valent cluster cations to unreactive low- and high-valent vanadium compounds. The only exception is mononuclear VO_2^+, which shows a significantly larger efficiency for the $^{16}O/^{18}O$ exchange despite a high formal valence (*f.v.* = 5). The latter finding can be rationalized by the consideration that the simplest, high-valent vanadium oxide ion, VO_2^+, provides only reactive sites for $^{16}O/^{18}O$ exchange, namely two vanadyl units; furthermore, these are most easily accessible by the neutral water molecule in comparison to the larger clusters. Interestingly, VO^+ and $V_3O_4^+$ having the same valence of the metal atom (*f.v.* = 3.0) show different reaction behavior in the IMR with $H_2{}^{18}O$: The trinuclear species $V_3O_4^+$ can still extrude an oxygen atom from water, whereas the mononuclear ion VO^+ shows no signals indicative of oxygen exchange above the noise level; this is consistent with the low reactivity of VO^+ toward water as reported earlier.[7]

The low-valent, dinuclear cluster cation $V_2O_2^+$ does not bear terminal vanadyl units. This view is consistent with the absence of a signal at Δm = +2, which would indicate the occurrence of $^{16}O/^{18}O$ exchange. Likewise, the coordinatively saturated cluster ions with high formal valences of the metal, like $V_3O_7^+$ or $V_4O_{10}^+$, do not show isotopic exchange of oxygen atoms as well (Figure 1). Further, note that the $^{16}O/^{18}O$ exchange of $V_2O_3^+$ has to compete with the occurrence of a net oxygen-atom uptake as described above.

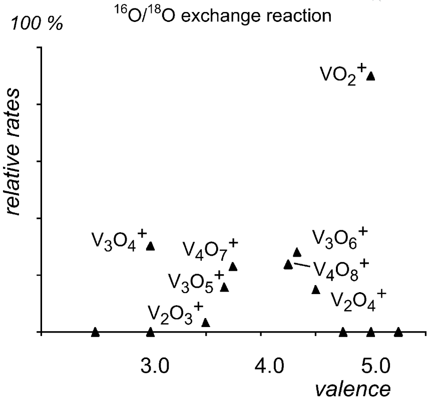


Figure 1. Relative rates of the reaction channel for the $^{16}O/^{18}O$ exchange as a function of the formal valence of vanadium in the $V_mO_n^+$ clusters.

IMRs of $V_mO_n^+$ with Molecular Oxygen

The IMRs of $V_mO_n^+$ clusters with O_2 (Table 2) include several reaction channels that can be grouped into three different categories: (1) A net uptake of one oxygen atom (Δm = +16) leads to the formation of $V_mO_{n+1}^+$. (2) Formal association of molecular oxygen to the cluster occurs (Δm = + 32), which is attributed to the formation of $V_mO_{n+2}^+$. (iii) Cluster degradation is observed to produce vanadium oxide cations upon loss of smaller, neutral vanadium oxide units.

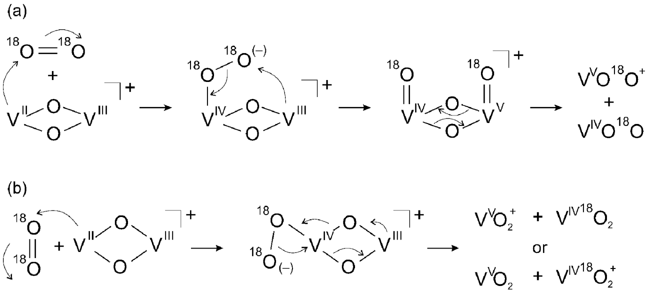
Table 2. Product ions, branching ratios (*BR* with ΣBR_i = 100), relative rate constants (k_{rel}), and formal valences of the vanadium atoms in the clusters (*f.v.*) in the IMRs of $V_mO_n^+$ cations with molecular oxygen [$p(O_2) = 2.0\times10^{-4}$ mbar].

$V_mO_n^+$	*f.v.*	k_{rel}	Product ions				
			VO^+	VO_2^+	$V_2O_4^+$	$V_mO_{n+1}^+$	$V_mO_{n+2}^+$
VO^+	3.00	n.r.[a]					
VO_2^+	5.00	n.r.[a]					
$V_2O_2^+$	2.50	25	24	76			
$V_2O_3^+$	3.50	50				100	
$V_2O_4^+$	4.50	n.r.[a]					
$V_3O_4^+$	3.00	50	54	5	41		
$V_3O_5^+$	3.67	50		32	1	1	66
$V_3O_6^+$	4.33	10				8	92
$V_3O_7^+$	5.00	n.r.[a]					
$V_4O_6^+$ [b]	3.25	60	38	2			55
$V_4O_7^+$	3.75	100		16	2		82
$V_4O_8^+$	4.25	70				2	98
$V_4O_9^+$	4.75	50					100
$V_4O_{10}^+$	5.25	n.r.[a]					

[a] n.r. = no reaction. [b] $V_4O_6^+$ leads to additional cluster degradation to produce $V_2O_3^+$ (BR = 5%).

For the low-valent, oxygen-deficient vanadium oxide cluster cations, such as $V_2O_2^+$, $V_3O_4^+$, and $V_4O_6^+$, degradation of the cluster predominates, which ultimately yields the mononuclear oxide ions VO^+ and VO_2^+ and the dinuclear species $V_2O_4^+$ concomitant with smaller, neutral vanadium oxide units. Such a behavior involving oxidative degradation of the clusters was previously reported by Engeser et al.[28] for several other low-valent vanadium oxide cluster cations. Interestingly, IMRs with $^{18}O_2$ reveal that the fragmentation of the vanadium oxide cluster cations results in smaller ionic fragmentation products containing oxygen-labeled moieties.

As an example, let us refer to the reaction of the dinuclear cluster ion $V_2O_2^+$ with molecular oxygen. Fragmentation of $V_2O_2^+$ leads to the generation of VO^+ and VO_2^+ and the respective neutral vanadium oxide units. The oxygen-labeling experiment results in the production of VO^+ and $V^{18}O^+$ in a ratio of 1:1, as well as to the formation of VO_2^+, $VO^{18}O^+$, and $V^{18}O_2^+$ in a ratio of 1.2:4:1. Accordingly, fragmentation cannot occur directly, but most likely proceeds via an intermediate association complex, $V_2O_2(^{18}O_2)^+$, with subsequent rearrangement to $V_2O_4^+$ with two μ-oxido bridges; this is followed by fragmentation into neutral and charged mononuclear vanadium dioxide. In Scheme 2, a suggestion is made for a fragmentation pathway in which (a) the oxidant attacks $V_2O_2^+$ from top (or bottom) of the cluster cation to form a superoxido ligand that is then attacked by the second vanadium atom of the cluster to bring about O−O bond cleavage. Fragmentation of the cluster cation eventually will generate $VO^{18}O^+$ and $VO^{18}O$ (Scheme 2a). Pathway (b) proceeds by attack of molecular oxygen to the side of the lower-valent vanadium atom in $V_2O_2^+$ to form also a superoxido ligand that attacks the vanadium center and finally leads to cluster degradation to produce $VO_2/V^{18}O_2^+$ and $VO_2^+/V^{18}O_2$. According to the branching ratio, fragmentation pathway (a) is involved twice as often as pathway (b). The oxygen-saturated clusters, on the other hand, for instance $V_3O_7^+$ and $V_4O_{10}^+$, do not react with molecular oxygen.



Scheme 2. Proposed fragmentation pathway of $V_2O_2^+$ upon collision with $^{18}O_2$ to produce (a) mixed isotopically labeled moieties, $VO^{18}O^+$and $VO^{18}O$ and (b) isotopically pure light and heavy vanadium dioxides, VO_2^+ and $V^{18}O_2$ (or VO_2 and $V^{18}O_2^+$).

Although the net uptake of one oxygen atom by $V_3O_5^+$, $V_3O_6^+$, and $V_4O_8^+$ occurs with rather low efficiency, it corresponds to the dominant reaction channel with $V_2O_3^+$ (*BR* = 100%, Table 2). Labeling experiments with $^{18}O_2$ show that the IMR of $V_2O_3^+$ with $^{18}O_2$ also leads to isotope exchange of a light oxygen atom (^{16}O) by dioxygen to form $V_2O_2{}^{18}O_2^+$ as well as to uptake of one ^{18}O atom to produce $V_2O_3{}^{18}O^+$. Both reaction channels appear in a ratio of about 2:1. The fact of uptake of one oxygen atom by $V_2O_3^+$ implies that the bond dissociation energy $D(V_2O_3^+–O)$ must exceed $D(O–O) = 498\ kJ·mol^{-1}$.

The IMRs of the vanadium oxide cluster cations with $^{18}O_2$ reveal several other interesting features. $^{16}O/^{18}O$ exchange reactions only occur with VO^+, $V_3O_6^+$, and $V_4O_8^+$. As an example, Figure 2 shows the relevant part of the product-ion mass spectrum for $^{18}O_2$ activation in the IMR of $V_4O_8^+$. Clearly, for $V_4O_8^+$ up to five oxygen atoms in the cluster are replaced by ^{18}O at a pressure of around $p(^{18}O_2) = 2 \times 10^{-4}$ mbar. Similar results were obtained for $V_3O_6^+$ (Table 3).

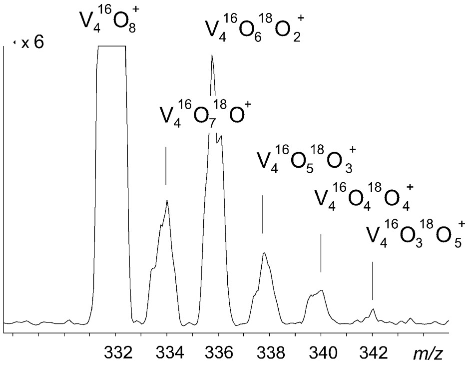


Figure 2. IMR of $V_4O_8^+$ with isotopically labeled molecular oxygen [$p(^{18}O_2) = 2 \times 10^{-4}$ mbar] focusing on the part that is indicative for $^{16}O/^{18}O$ exchange reactions.

Table 3. Isotope patterns (normalized to Σ = 100) of the product ions formed upon $^{16}O/^{18}O$ exchange of $V_3O_6^+$ and $V_4O_8^+$ in the IMRs with $^{18}O_2$ at $p(^{18}O_2) = 2 \times 10^{-4}$ mbar.

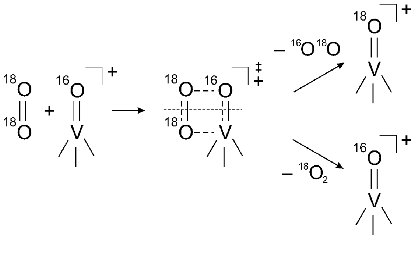
	$V_m{}^{16}O_{n-1}{}^{18}O$	$V_m{}^{16}O_{n-2}{}^{18}O_2$	$V_m{}^{16}O_{n-3}{}^{18}O_3$	$V_m{}^{16}O_{n-4}{}^{18}O_4$	$V_m{}^{16}O_{n-5}{}^{18}O_5$
$V_3O_6^+$	30	35	24	7	4
$V_4O_8^+$	20	59	15	4	2

As already demonstrated for the IMRs with $H_2{}^{18}O$, the mononuclear species do not follow the general trends observed for the vanadium oxide cluster cations: whereas the simplest vanadium oxide ion, VO^+, activates molecular oxygen, VO_2^+ does not result in any product ions upon interaction with O_2. Evidently, VO^+ exchanges one light oxygen atom toward ^{18}O to form $V^{18}O^+$. Interestingly, all other cluster cations examined do not form any reaction products that can be assigned to the occurrence of $^{16}O/^{18}O$ exchange reactions.

The occurrence of oxygen-atom exchange exclusively for the cluster cations $V_3O_6^+$ and $V_4O_8^+$ can be explained in the following way. As demonstrated in the IMR of $V_mO_n^+$ with $H_2{}^{18}O$, vanadium oxide clusters of medium valence are capable to activate V–O bonds. With increasing valence, the O atom affinity decreases and therewith the general tendency to activate molecular oxygen, that is, the high-valent vanadium oxide clusters, such as $V_3O_7^+$ and $V_4O_{10}^+$, do not react anymore with oxidizing agents. In contrast, the low-valent vanadium oxide clusters show oxygen-atom uptake and/or undergo cluster degradation. Hence, degenerate isotopic exchange reactions, like for $V_3O_6^+$ and $V_4O_8^+$, emerge if the cluster cations balance well the O_2 activation ability and the susceptibility to lose an oxygen atom from the cluster. In addition to mere aspects of valence states, structure-specific aspects also might come into play, which prevent, for example, the occurrence of $^{16}O/^{18}O$ exchange for the corresponding dinuclear cluster cation $V_2O_4^+$. In this respect, the significantly large V–O bond dissociation energy determined for $V_2O_4^+$ [$D(V_2O_3^+–O) > 498\ \mathrm{kJ\,mol^{-1}}$] by IMR of $V_2O_3^+$ with molecular oxygen might also account for the absence of oxygen isotopic exchange in $V_2O_4^+$.

Recurring to the three processes proposed by Klier et al.[24] and Muzykantov et al.[25] we resume: $^{16}O/^{18}O$ exchange reactions can proceed without direct involvement of lattice oxygen (R^0-mechanism), and only one O atom of O_2 is replaced by the surface oxygen of the metal oxide (R^1-mechanism) and/or both atoms of a single oxygen molecule are exchanged (R^2-mechanism). According to the branching ratios obtained for $V_3O_6^+$ and $V_4O_8^+$ in the reaction with $^{18}O_2$, one can clearly rule out the exclusive occurrence of the R^2-mechanism (Table 3 and Figure 2). Furthermore, as the experiment is performed at room temperature, the R^0-mechanism without involvement of the cluster cation can be excluded as well. Thus, the R^1-mechanism with stepwise replacement of the oxygen atoms appears most likely.

A possible reaction mechanism for the $^{16}O/^{18}O$ exchange reaction at a vanadyl unit in the cluster cation is illustrated in Scheme 3. Most likely, in a formal [2+2] addition one ^{18}O atom is transferred to the vanadium atom of the vanadyl unit and the second ^{18}O atom attaches to the oxygen atom in the vanadyl unit. Then, in a consecutive step, either $^{16}O^{18}O$ or $^{18}O_2$ are released to afford $V^{18}O$ and $V^{16}O$ moieties, respectively. Particularly remarkable is the fact that an interaction of both cluster cations, $V_3O_6^+$ and $V_4O_8^+$, with molecular oxygen leads to an exchange of up to five lattice oxygen atoms. This feature indicates that, in addition to the above described mechanism, also bridging V–O–V units can be exchanged.



Scheme 3. Possible scenario for $^{16}O/^{18}O$ exchange occurring at a VO^+ unit in the reaction with $^{18}O_2$.

Conclusions

The reactions of mass-selected vanadium oxide cluster cations $V_mO_n^+$ with water result in association to the corresponding adduct ions or in degenerate O-atom exchange, where the latter is probed by means of ^{18}O labeling. The ability for $^{16}O/^{18}O$ exchange is particularly pronounced for those clusters in which vanadium exhibits a medium valence state, whereas high-valent clusters, such as $V_3O_7^+$, $V_4O_9^+$, and $V_4O_{10}^+$, as well as the low-valent vanadium oxides $V_2O_2^+$ and VO^+ cannot activate water. The mononuclear species VO_2^+ forms an exception, as this metal oxide ion is high-valent and constitutes the most reactive ion with respect to $^{16}O/^{18}O$ exchange.

The reactions with molecular oxygen exemplify pronounced size-selective effects of the vanadium oxide cluster cations. For instance, only those cluster cations that well balance the O_2 activation ability and the susceptibility to lose an oxygen atom, such as $V_3O_6^+$ and $V_4O_8^+$, bring about oxygen-isotope exchange reactions. The occurrence of sequential exchange reactions of up to five oxygen atoms further indicate that $V_3O_6^+$ and $V_4O_8^+$ both provide active sites in the cluster to interact with molecular oxygen promoting the activation of the adjacent vanadyl bond as well as of bridging V–O–V bonds. Furthermore, it is shown that IMRs of low-valent vanadium oxide cluster cations with O_2 are accompanied by cluster degradation to produce smaller vanadium oxide units. Labeling experiments show that fragmentation of the cluster does not occur directly, but most likely upon formation of an association complex with the reactant.

Finally, the results for both probe molecules, H_2O and $^{18}O_2$, strongly suggest that, unlike other ionization methods, the generation of $V_mO_n^+$ cluster cations by electrospray ionization of molecular clusters does not lead to the formation of loosely bounded dioxygen complexes.

Experimental Section

Ion/molecule reactions (IMRs) were investigated by using a VG-BioQ mass spectrometer that consists of an electrospray ionization (ESI) source combined with a tandem mass spectrometer of QHQ configuration (Q = quadrupole, H = hexapole).[29] The hexanuclear (methoxido)oxidovanadium cluster $V_6O_7(OCH_3)_{12}$ used as precursor compound[30] was dissolved in CD_3OD and sprayed under harsh ESI conditions in order to obtain the smaller vanadium oxide clusters $V_mO_n^+$ (m = 1–4; n = 1–10) as described in detail elsewhere.[15a,21] To this end, a solution of the precursor was introduced into the ESI source by using fused silica tubing (75 µm ID) at a flow rate of about 5 µL min^{-1} and a source temperature of 90 °C. The cone voltage was kept at about 190 V to maximize the fragmentation of the precursor in order to increase the signals of the desired smaller clusters.[15a,21] All data were collected and averaged over at least 20 scans and up to 100 scans for weaker signals. The bimolecular reactivities of the mass-selected metal oxide cluster ions toward water and molecular oxygen are studied by introducing the oxidant at pressures of $(0.5–2) \times 10^{-4}$ mbar at a collision energy set to nominally 0 eV, which in conjunction with the ca. 0.4 eV kinetic energy width of the parent ion at peak half height[29a] allow the investigation of quasithermal reactions, as demonstrated previously.[26,31] Although the use of drastic ionization conditions to induce substantial degradation of the precursor cluster to bare $V_mO_n^+$ ions is associated with substantial heating of the ions, they afterwards pass several regions of relatively large pressures (up to a few mbar), which provide an efficient cooling of the ions. This conclusion has been reached from previous studies of known ion/molecule reactions in the VG BioQ,[32] and is specifically supported by comparison of the results for $V_mO_n^+$ ions reacting with various

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small hydrocarbons, in which general agreement was attained for the data obtained with the present set-up and earlier data from Bell et al. by using an entirely different kind of mass spectrometer.[9i]

Given the limited mass resolution of quadrupole-based mass spectrometers, characterization and generation of pure vanadium clusters was more difficult, as they may contain isobaric oxido- and/or methanol ligands. An exchange of the methoxido ligands in the precursor molecule $V_6O_7(OCH_3)_{12}$ to OCD_3 groups circumvents this ambiguity, which has been described in-depth elsewhere.[15a]

The IMRs with water and $^{18}O_2$ also lead occasionally to the production of association complexes with light molecular oxygen, which can be attributed to the presence of impurities in the vacuum system. These products are not mentioned any further, but are acknowledged in the analysis of the data. The branching ratios (*BR*) were determined from the intensity ratios of the product ions normalized to Σ(products) = 100, where possible secondary reaction products are summed into the respective primary channels. A quantitative measurement of the reaction delay is not possible for experiments accomplished at the VG BioQ mass spectrometer and thus no absolute rate constants are given here. However, relative rate constants, k_rel, can be determined that combine experimental rate constant and reaction delay. Consequently, k_rel is calculated according to $k_\text{rel} = (-1/[\text{B}]) \ln(I/\Sigma I_\text{i})$ with [B] as the partial pressure of the neutral substrate B, that is, water or molecular oxygen, I as the signal intensity of the parent ion, and ΣI_i is related to the sum of all intensities. The relative rate constants can be converted into absolute values by reference to known ion/molecule reactions,[32,33] but this effort has not been undertaken in this survey of vanadium oxide cluster ions.

In addition, the $V_mO_n^+$ cluster ions formed by ESI were also characterized by a series of collision-induced dissociation (CID) experiments. To this end, the mass-selected $V_mO_n^+$ ions were collided with xenon admitted to the hexapole at variable collision energies. In brief, cluster degradation through loss of neutral V_mO_n units prevails in these CID experiments, leading down to the quasiterminal mononuclear species VO^+, whose formation as a cationic fragment is preferred by the particularly low ionization energy of neutral VO (7.24 eV).[34] Moreover, the energies required to induce a significant amount of fragmentation are rather high (>5 eV), which is consistent with previous data for binary metal oxide cluster cations.[35] The CID experiment of the high-valent $V_4O_{10}^+$ leads to a considerable amount of O_2 loss. According to the latter outcome, we cannot entirely exclude the existence of $V_4O_8(O_2)^+$. However, O_2 loss is only observed for larger collision energies (>8 eV), which is consistent with the calculated thermochemistry of $V_4O_{10}^+$ predicting an energy for its dissociation to O_2 and $V_4O_8^+$ around 420 kJ mol^{-1}.[17] Instead, loss of the weakly coordinated dioxygen ligand from the complex $V_4O_8(O_2)^+$ should already appear at a lower threshold (44 kJ·mol^{-1}, i.e. 0.5 eV).[17]

All unlabeled and labeled reagents are used as purchased and introduced into the mass spectrometer by conventional vacuum techniques. Deuteration of $V_6O_7(OCH_3)_{12}$ was achieved by simple dissolution of the precursor in a 100-fold excess of CD_3OD followed by one-week storage at ambient temperature. After this treatment, more than 95% deuteration is achieved, as probed by ESI mass spectrometry.[21]

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