

Gas-Phase Oxidation of Isomeric Butenes and Small Alkanes by Vanadium-Oxide and -Hydroxide Cluster Cations

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Bare vanadium-oxide and -hydroxide cluster cations ($V_mO_nH_o^+$, $m = 2-4$, $n = 1-10$, $o = 0, 1$) were generated by electrospray ionization in order to examine their intrinsic reactivity toward isomeric butenes and small alkanes using mass spectrometric techniques. Two of the major reactions described here concern the activation of C–H bonds of the alkene/alkane substrates resulting in the transfer of two hydrogen atoms and/or attachment of the dehydrogenated hydrocarbon to the cluster cations; these processes are classified as oxidative dehydrogenation (ODH) and dehydrogenation, respectively. For the dehydrogenation of butene, it evolved as a general trend that high-valent clusters prefer ODH resulting in the addition of two hydrogen atoms to the cluster concomitant with elimination of neutral butadiene, whereas low-valent clusters tend to add the diene with parallel loss of molecular hydrogen. Deuterium labeling experiments suggest the operation of a different reaction mechanism for $V_2O_2^+$ and $V_4O_{10}^+$ compared to the other cluster cations investigated, and these two cluster cations also are the only ones of the vanadium-oxide ions examined here that are able to dehydrogenate small alkanes. The kinetic isotope effects observed experimentally imply an electron transfer mechanism for the ion–molecule reactions of the alkanes with $V_4O_{10}^+$.

Introduction

Much of the world's need for both carbon-based materials and its energy demand are based on petroleum or natural gas. To efficiently convert these resources, which are primarily composed of alkanes, into more useful materials, catalysts for selective C–H bond activation need to be employed.¹ Despite the rapid strides made in catalyst development in the 20th century, in which many catalysts requiring noble metals were replaced by 3d elements, today's catalysts are still not sufficiently active enough to bring about selective, partial oxidation of alkanes.

Vanadium oxides represent an important class of transition metal catalysts used in chemical industry, for instance, in the production of SO_3 from SO_2 , for the conversion of propane to propene, and in 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, while it is quite likely that oxygen vacancies are present on the surfaces of vanadium catalysts, their precise catalytic function in the active site yet 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,^{7–14} with the aim of obtaining more insightful information about structure/reactivity correlations, cluster-size effects, and the role of formal and real charge. Gas-phase studies can provide direct insight into the intrinsic properties of the clusters and moreover also may deepen the understanding of the relevant reaction mechanism by means of combining mass spectrometric experiments with labeling studies and theoretical approaches.^{14,15} Electrospray ionization mass spectrometry (ESI-MS)¹⁶ has opened up new horizons in the analysis of inorganic and

organometallic systems^{17,18} and also provides access to vanadium-oxide and -hydroxide cluster ions ($V_mO_nH_o^{+/-}$) if appropriate precursors are employed.^{19,20} As reported previously, VO_2^+ dehydrogenates ethane to yield the $VO_2H_2^+$ cation concomitant with ethene being formed as a neutral molecule.^{21,22} In an extension to these earlier studies of mononuclear cations,^{21–23} reactions of larger vanadium-oxide and -hydroxide clusters are reported here. Calculations of the bond dissociation energies of some clusters have been performed for the radical cations $V_2O_5^+$ and $V_4O_{10}^+$ and the closed-shell cluster ion $V_3O_7^+$ by Sauer and co-workers.^{5a–c}

Experimental Methods

Ion–molecule reactions (IMRs) are investigated using a quadrupole-based mass spectrometer equipped with an electrospray ionization source as described elsewhere.²⁴ The precursor compound $V_6O_7(OCH_3)_{12}$ has been synthesized in the laboratory of Prof. H. Hartl at the Freie Universität Berlin according to well-known literature procedures.²⁰ This hexanuclear methoxovanadium cluster is dissolved in an excess of deuterated methanol to exchange the methoxo ligands to fully deuterated ones which is achieved after 1 week of storage in CD_3OD at ambient temperature.¹⁹ The resulting solution is introduced into the ESI source using fused silica tubing (75 μm ID) at a flow rate of less than 5 $\mu L/min$ and a source temperature of 90 °C. Under harsh ESI conditions, smaller vanadium-oxide and -hydroxide clusters of the general formula $V_mO_nH_o^+$ ($m = 2-4$, $n = 1-10$, $o = 0, 1$; or the deuterated variants) are obtained.¹⁹ The cone voltage is kept at about 190 V to maximize the fragmentation of the precursor in order to increase the signals of the desired smaller vanadium-oxide clusters. All data are collected and averaged over at least 20, and for weaker signals up to 100, scans.

The investigated clusters are characterized by collision-induced dissociation (CID) experiments brought about by mass

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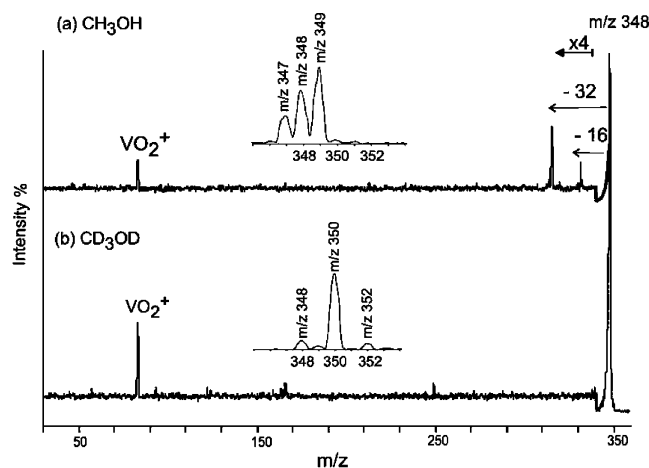
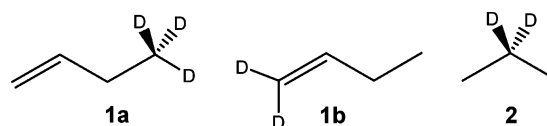


Figure 1. CID spectra of m/z 348 that derives from (a) $V_6O_7(OCH_3)_{12}$ in CH_3OH and (b) $V_6O_7(OCD_3)_{12}$ in CD_3OD at a collision energy of 40 eV. The insets show the corresponding mass regions of ions evolving from the ESI source.

selection of the ions of interest using Q1, followed by interaction with xenon gas at pressures on the order of 2×10^{-4} mbar in the hexapole at a collision energy of 40 eV (E_{lab}), while Q2 was scanned to monitor the ionic products. IMRs at quasi-thermal energies were probed in the same manner except that E_{lab} was nominally set to 0 eV; the width of the kinetic energy distribution in the hexapole amounts to ~ 0.4 eV at half peak height. In addition, the $V_mO_nH^+$ cluster cations are investigated by IMRs with methanol, which indicate the presence of vanadium-hydroxide clusters ($V_mO_{n-1}(OH)^+$) rather than vanadium-hydride clusters ($HV_mO_n^+$).²⁵ Likewise, the bimolecular reactivity of the respective clusters toward isomeric butenes as representatives of small alkenes as well as toward alkanes is studied by introducing these neutral reagents into the hexapole at similar pressures which approximately corresponds to single-collision conditions.

A peculiarity of the present system arises from the fact that dioxygen and methanol have the same nominal mass. Given the limited mass resolution of a quadrupole mass spectrometer, a characterization of the vanadium clusters therefore is more difficult, as they may contain isobaric dioxo and/or methanol ligands. Thus, nontrivial superposition prevents the elucidation of accurate reactivity data for the respective ions. However, an exchange of the methoxy ligands in the precursor molecule $V_6O_7(OCH_3)_{12}$ to OCD_3 groups facilitates largely the assignment, because most isobaric overlaps are prevented. A comparison of the abundances of the vanadium-oxide ions generated from $V_6O_7(OCH_3)_{12}$ in CH_3OH and of those generated from CD_3OD solution demonstrates the degree of interferences (Figure 1). For an illustration, let us consider the signals at m/z 347, 348, and 349. The signal at m/z 347 produced by ESI from a CH_3OH solution of the sample can in principle be assigned to $V_4O_{7-2n}(CH_3OH)_n(OCH_3)^+$ ($n = 0-3$). As this signal is quantitatively shifted to m/z 350 when the ESI spectrum is taken from a CD_3OD solvent, there is only one methoxy unit present in the cluster; that is, one is dealing with $V_4O_7(OCD_3)^+$. Similarly, the signals at m/z 348 and 349 are due to $V_4O_{9-2n}(CH_3OH)_n^+$ and $V_4O_{9-2n}H(CH_3OH)^+$ ($n = 0-4$), respectively, and a more specific assignment is possible upon the use of CD_3OD as a solvent. The abundance of the signal at m/z 348 in CD_3OD solution pales in comparison with that formed from $V_6O_7(OCH_3)_{12}$ in CH_3OH and suggests interference of $V_4O_9^+$ (m/z 348) and $V_4O_7(CD_3OD)^+$ (m/z 352). On the other hand, the signal at m/z 349 taken in CH_3OH is almost entirely

CHART 1: Deuterated Hydrocarbons



shifted to the deuterated species at m/z 350 to produce $V_4O_9D^+$. Most notable in the present context is the fact that deuteration allows essentially pure beams of $V_mO_nD_o^+$ clusters to be generated.

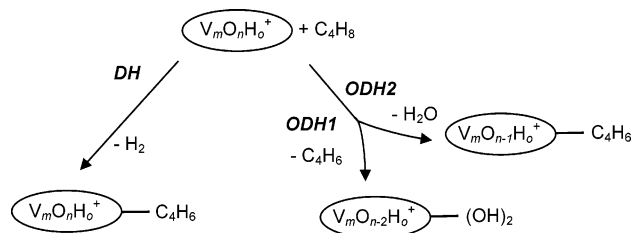
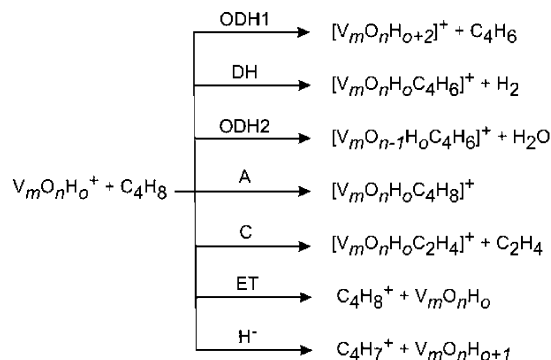
CID experiments further confirm this conclusion for m/z 348: The mass-selected ion beam generated from a CD_3OD solution of the $V_6O_7(OCD_3)_{12}$ precursor only results in the formation of vanadium oxides such as VO_2^+ (Figure 1b). However, CID experiments of m/z 348 from a CH_3OH solution lead to additional losses of 16 and 32 mass units, which can be assigned to the eliminations of methane and methanol, respectively (Figure 1a). Both results suggest the existence of a mixture of $V_4O_9^+$ and $V_4O_7(CH_3OH)^+$ ions in CH_3OH solution.¹⁹ In CD_3OD solution, however, the latter ions do not interfere anymore because they are shifted 4 mass units higher.

In addition to the major reaction channels, discussed below, the formation of several minor products is observed occasionally and can be attributed to the presence of impurities in the vacuum system, such as association reactions with water and dioxygen, respectively. These products are acknowledged in the analysis of the data but are not explicitly mentioned any further; rather, we focus on dehydrogenation reactions of isomeric butenes and alkanes by the cluster ions.

All unlabeled and labeled (Chart 1) reagents are used as purchased with the exception of **1a** which was synthesized using an established procedure.²⁶ The introduction into the mass spectrometer was accomplished by conventional vacuum techniques. Deuteration of $V_6O_7(OCH_3)_{12}$ was achieved by dissolving the compound in a 100-fold excess of CD_3OD followed by 1 week of storage at ambient temperature.¹⁹ After this treatment, more than 95% deuterium incorporation is achieved as probed by ESI mass spectrometry.

Results and Discussion

In the present work, ESI is used to generate di-, tri-, and tetranuclear vanadium-oxide and -hydroxide cations as gas-phase species, thus allowing their reactivities and properties to be examined with a quadrupole-based mass spectrometer. To this end, ion-molecule reactions with isomeric butenes and small alkanes were examined in order to elucidate mechanistic details concerning the oxidative dehydrogenation (ODH) as well as the related dehydrogenation (DH) process. In the overall transformation of ODH, a formal reduction of the metal center occurs ($V_mO_nH_o^+ + 2H^+ + 2e^- \rightarrow [V_mO_nH_{o+2}]^+$), which is brought about by a two-proton and two-electron transfer in the course of the oxidation of an alkene to a diene and the conversion of an alkane to an alkene, respectively, for example, $C_4H_8 \rightarrow C_4H_6 + 2H^+ + 2e^-$. Two alternative product channels evolve from ODH: Either butadiene is lost as a neutral concomitant with two hydrogen atoms being transferred to the cluster cations to form $[V_mO_nH_{o+2}]^+$ (ODH1) or water may be lost as a neutral molecule while the unsaturated hydrocarbon fragment remains at the metal center to afford $[V_mO_{n-1}H_oC_4H_6]^+ + H_2O$ (ODH2). In marked contrast, DH occurs without reduction of the metal center; rather, transfer of the dehydrogenated hydrocarbon to the cluster is accompanied with the evaporation of dihydrogen (Scheme 1).

SCHEME 1: Product Channels for the Dehydrogenation of Butene by $V_mO_nH_o^+$ Concomitant with the Release of Dihydrogen, Water, or Butadiene as Neutral Molecules

SCHEME 2: Primary Products for the Reactions of $V_mO_nH_o^+$ with Isomeric Butenes (for Details, See Table 1)


Alkenes. The IMRs of mass-selected vanadium-oxide and -hydroxide ions with 1-butene, *cis*-butene, *trans*-butene, and *iso*-butene lead to up to seven major product channels depending on the nature of the cluster (Scheme 2, Table 1). For the majority of the clusters, the experiments result in the gain of 56 mass units which is considered as association (A) of the cluster ion with an intact butene molecule to afford $[V_mO_nH_oC_4H_8]^+$. In addition, IMRs of $V_mO_nH_o^+$ also lead to increases by 2 and 54 mass units, which are assigned to ODH1 and DH of the olefin, respectively, yielding either $[V_mO_nH_{o+2}]^+$ or a $[V_mO_nH_oC_4H_6]^+$ cation. Furthermore, transfer of butene to the cluster cations concomitant with loss of water is observed as a minor channel (ODH2). Moreover, upon reaction of $V_mO_nH_o^+$ with butene, for some cluster ions, weak signals are observed which are indicative of C–C bond cleavages (C). For two vanadium oxides, electron transfer (ET) and hydride transfer (H^-) are observed as well to form $C_4H_8^+$ and $C_4H_7^+$ concomitant with the corresponding neutral species $V_mO_nH_o$ and $V_mO_nH_{o+1}$, respectively.

Unfortunately, the experimental setup does not allow for a further structural characterization of the reaction products formed in the hexapole collision cell. In particular, we cannot distinguish between mere association complexes of the type $[V_mO_nH_o(C_4H_8)]^+$ and addition products that contain newly formed covalent bonds in the product ion, that may result from bond activation of the incoming C_4H_8 ligand. For the time being, molecular addition is not considered as a bond activation process in the comparative analysis of the data but rather considered as a simple association.

Illustrations for the diverse reactivities of the vanadium-oxide cluster ions are given in Figure 2 for the ion–molecule reaction of $V_3O_7^+$ with *cis*-butene and for $V_4O_{10}^+$ with *cis*-butene and 1-butene (see also Table 1).

In the ion–molecule reactions with butenes regarding ODH, the most reactive cluster cations (with decreasing reactivity) are found to be the high-valent vanadium-oxide ions $V_3O_7^+$, $V_2O_4^+$, $V_4O_{10}^+$, and $V_3O_6^+$, respectively. In contrast, the low-valent

cluster oxide cations are completely unreactive with respect to the formal uptake of two hydrogen atoms (ODH1). This conclusion becomes obvious upon inspection of Figure 3a in which the efficiency of this particular reaction for all four butene isomers is plotted versus the formal valence of vanadium in the cluster cations: Quite clearly, the ODH activity increases with the valence of the vanadium.

Whereas oxidative dehydrogenation generally predominates over mere dehydrogenation, some DH activity ($V_mO_nH_o^+ + C_4H_8 \rightarrow [V_mO_nH_oC_4H_6]^+ + H_2$) is observed for several of the low-valent clusters. Interestingly, DH shows the opposite behavior with formal valence as compared with ODH: Clearly, the lower the formal valence of the metal in cluster ions, the higher the DH activity, as reflected by uptake of C_4H_6 concomitant with elimination of dihydrogen as a neutral molecule (Figure 3b).

The observed differences in DH and ODH for the low- and high-valent cluster ions are consistent with qualitative aspects of basic bonding concepts. Thus, low-valent ions having occupied d orbitals are suitable for an interaction with the empty π^* orbital of the alkene ligands according to a Dewar–Chatt–Duncanson model²⁸ and hence tend to prefer the DH process. In contrast, high-valent metal-oxo cations, such as $V_3O_7^+$, for instance, cannot provide occupied d orbitals; rather, due to the large number of electronegative oxo ligands, they exhibit a higher H-atom affinity, thus favoring ODH. This result is supported by the work of Asmis et al.^{11b} in which the structures of divanadium-oxide cluster cations were investigated: The DH preferring low-valent cluster cations, like $V_2O_2^+$ and $V_2O_3^+$, contain two or at least one vanadium atom without oxo groups, whereas the ODH preferring cations, like $V_2O_4^+$ and $V_2O_5^+$, are found to provide at least one or two vanadyl groups, respectively. Equivalently, the most reactive cation $V_3O_7^+$ concerning ODH is calculated to provide even three vanadyl groups for H_2 uptake.⁵

Taking the two C–H bond activation processes together, a summation of the ODH and DH reactivities of each of the four isomeric butenes demonstrates that 1-butene exhibits the highest reactivities among the C_4 alkenes investigated. Isomeric *cis*- and *trans*-butenes show, not surprisingly, very similar reactivities and have only about 70 and 80%, respectively, of the ODH and DH reactivities observed for 1-butene. *iso*-butene does not undergo DH by any of the vanadium-oxide and -hydroxide clusters and exhibits an ODH activity of only about 8%. This finding is consistent with the intuitive view that a linear C_4 skeleton may easily convert into a diene ligand, whereas 2-fold unsaturation of a branched C_4 unit is more difficult to realize.

Isotope-tracer studies with the deuterated 1-butenes $CD_3CH_2CHCH_2$ (**1a**) and $CH_3CH_2CHCD_2$ (**1b**) suggest different reaction mechanisms for the cations $V_2O_2^+$, $V_2O_4^+$, $V_2O_5^+$, and $V_4O_{10}^+$ on one hand as compared with the other reactive vanadium-oxide clusters investigated. ODH of these two isotopologues is associated with H/D equilibration, as indicated for the cations $V_2O_4^+$ and $V_2O_5^+$ by gains of 2 and 3 mass units²⁹ and for the cation $V_4O_{10}^+$ by 2, 3, and 4 mass units.³⁰ These results imply transfers of H_2 , HD, and D_2 . However, for all other vanadium-oxide cations studied here, a specific mass increase of 3 units is observed when reacted with **1a** and an increase of only 2 mass units occurs when reacted with **1b**, thus demonstrating selective 1,2-dehydrogenations at C(3)/C(4). Figure 4 shows the reactions of $V_3O_7^+$ and $V_4O_{10}^+$ with **1a** as an example with a clean uptake of HD by the former and nonselective ODH reactions by the latter clusters. Dehydrogenation of the two isotopically labeled 1-butenes by the low-valent $V_2O_2^+$ cation

TABLE 1: Normalized Intensities for the Seven Major Channels (ODH1, Oxidative Dehydrogenation Concomitant with the Loss of Butadiene; DH, Dehydrogenation; ODH2, Oxidative Dehydrogenation Concomitant with the Loss of Water; A, Molecular Addition; C, Carbon–Carbon Bond Cleavage; ET, Electron Transfer; H⁻, Hydride Transfer) upon Reaction of V_mO_n⁺ and V_mO_nD⁺ with 1-Butene, *cis*-Butene, *trans*-Butene, and *Iso*-Butene^{a-c}

	1-butene							<i>iso</i> -butene						
	ODH1	DH	ODH2	A	C	ET	H ⁻	ODH1	DH	ODH2	A	C	ET	H ⁻
V ₂ O ₂ ⁺		31									11			
V ₂ O ₂ D ⁺		17												
V ₂ O ₃ ⁺		5	3	21	11						30			
V ₂ O ₃ D ⁺		20		11										
V ₂ O ₄ ⁺	36		1	5	3						24			
V ₂ O ₄ D ⁺	1	3	2	16	1						21			
V ₂ O ₅ ⁺	10				4							3		
V ₂ O ₅ D ⁺			8	16						4	21			
V ₃ O ₄ ⁺		2		14							20			
V ₃ O ₄ D ⁺		4		10										
V ₃ O ₅ ⁺			2	21								28		
V ₃ O ₅ D ⁺				21							26			
V ₃ O ₆ ⁺	14			15							39			
V ₃ O ₆ D ⁺	1			31							19			
V ₃ O ₇ ⁺	54			6	7	3	14				25		4	7
V ₃ O ₇ D ⁺	8			31										
V ₄ O ₆ ⁺				25							22			
V ₄ O ₇ ⁺				37							26			
V ₄ O ₇ D ⁺				30							5			
V ₄ O ₈ ⁺				37							28			
V ₄ O ₈ D ⁺				28							27			
V ₄ O ₉ ⁺	12			23						1	36			
V ₄ O ₉ D ⁺	1			24							27			
V ₄ O ₁₀ ⁺	14		5	1	<i>d</i>	38	34	3		2			15	3
V ₄ O ₁₀ D ⁺				25		<i>e</i>					20		<i>e</i>	
	<i>cis</i> -butene							<i>trans</i> -butene						
	ODH1	DH	ODH2	A	C	ET	H ⁻	ODH1	DH	ODH2	A	C	ET	H ⁻
V ₂ O ₂ ⁺		19							21		2			
V ₂ O ₂ D ⁺		9							8		3			
V ₂ O ₃ ⁺		4	7	36	8				3	2	22	9		
V ₂ O ₃ D ⁺		16		9					14		8			
V ₂ O ₄ ⁺	29			7				35		1	1	1		
V ₂ O ₄ D ⁺		4	2	18				1	1		12	1		
V ₂ O ₅ ⁺				<i>f</i>				8			1	2		
V ₂ O ₅ D ⁺				26						7	13			
V ₃ O ₄ ⁺				14							14			
V ₃ O ₄ D ⁺				9					2	2	9			
V ₃ O ₅ ⁺			2	29						1	18			
V ₃ O ₅ D ⁺				19	2						17			
V ₃ O ₆ ⁺	18			12	1			18			6			
V ₃ O ₆ D ⁺	2			24				2			15			
V ₃ O ₇ ⁺	55			9	2	8	10	55			4		6	15
V ₃ O ₇ D ⁺	8			26				2			15			
V ₄ O ₆ ⁺				27							14			
V ₄ O ₇ ⁺				34							18			
V ₄ O ₇ D ⁺				28							21			
V ₄ O ₈ ⁺	1			28							19			
V ₄ O ₈ D ⁺				26							19			
V ₄ O ₉ ⁺	4			22				6			21			
V ₄ O ₉ D ⁺	1			23							16			
V ₄ O ₁₀ ⁺	11			1		100 ^g	13	14		21	2		74	14
V ₄ O ₁₀ D ⁺				19		<i>e</i>					17		<i>e</i>	

^a General equations for the seven major channels: ODH, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_{o+2}⁺ + C₄H₆; DH, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_oC₄H₆⁺ + H₂; ODH2, V_mO_nH_o⁺ + C₄H₈ → V_mO_{n-1}H_oC₄H₆⁺ + H₂O; A, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_oC₄H₈⁺; C, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_oC₂H₄⁺ + C₂H₄; E, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_o + C₄H₈⁺; H, V_mO_nH_o⁺ + C₄H₈ → V_mO_nH_{o+1} + C₄H₇⁺. The deuterated variants are listed here as the experiments are carried out in CD₃OD to eliminate superposition of CH₃OH and O₂; see text. ^b Other cations, such as V₃O₈⁺, V₃O₈D⁺, V₃O₉⁺, V₃O₉D⁺, and V₄O₆D⁺, are not included in the table, as IMRs indicate impurities due to unreactive isobaric interferences. ^c Experiments are carried out at equal pressures of butenes. ^d Further, loss of 16 and 14 mass units and addition of 14 mass units (with an intensity of 4, <1, and 4, respectively) are observed for the reaction of V₄O₁₀⁺ with 1-butene. ^e IMR of V₄O₁₀D⁺ with isomeric butenes resulted in addition in *m/z* 58, which can be viewed as a product that is formed due to electron transfer and subsequent transfer of deuterium (with an intensity of ~5). ^f Not measured. ^g Signal used for normalization.²⁷

is also associated with H/D equilibration, as indicated by mass gains of 56 and 57 which are assigned to the additions of the appropriate 1,3-butadiene isotopologues concomitant with losses of HD and H₂, respectively.²⁹ In contrast, the remaining low-

valent cations, that is, V₂O₃⁺, show a mass increase of 56 units with **1b**, suggesting a specific 1,2-dehydrogenation to form [V_mO_nH_oC₄H₄D₂]⁺ concomitant with the evaporation of neutral dihydrogen.

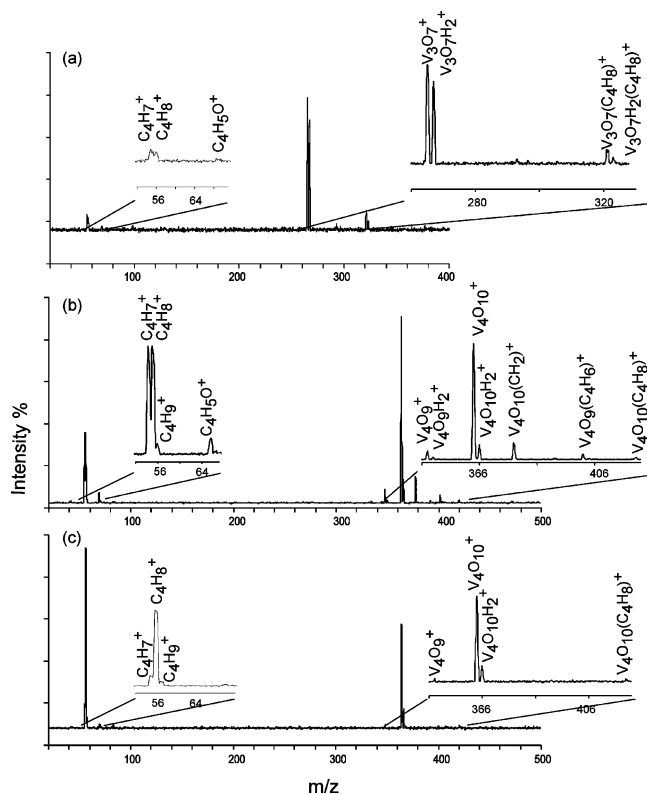


Figure 2. IMR of (a) $V_3O_7^+$ with *cis*-butene, (b) $V_4O_{10}^+$ with *cis*-butene, and (c) $V_4O_{10}^+$ with 1-butene. $p(\text{butene}) = 2.7 \times 10^{-4}$ mbar; collision energy adjusted to nominally 0 eV. The insets focus on the respective signals as discussed in the text.

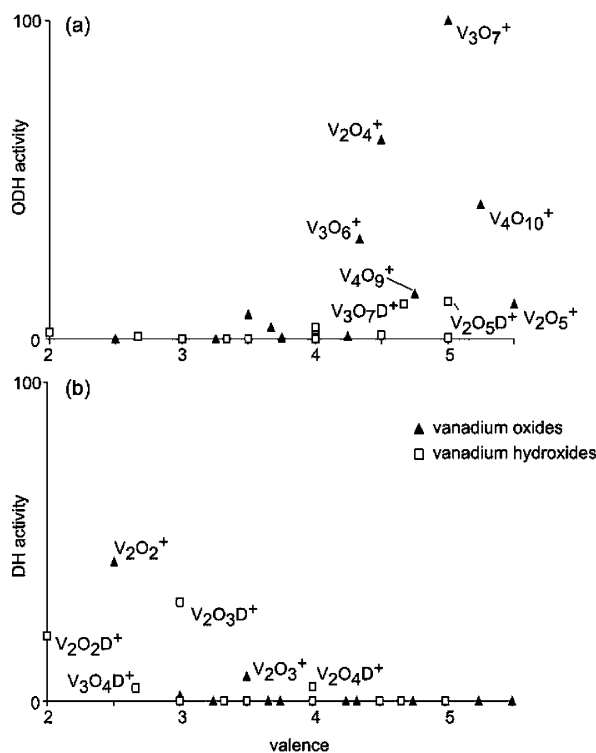


Figure 3. Sum of intensities of (a) H_2 uptake (ODH1) and loss of water (ODH2) and (b) addition of C_4H_6 (DH) for 1-butene, *cis*-butene, *trans*-butene, and *iso*-butene versus the formal valence of vanadium in the $V_mO_nH_o^+$ clusters.

As mentioned above, the reactions of the high-valent $V_3O_7^+$ and $V_4O_{10}^+$ vanadium-oxide cations with isomeric butenes also result in electron and hydride transfer.^{31,32} The former leads to

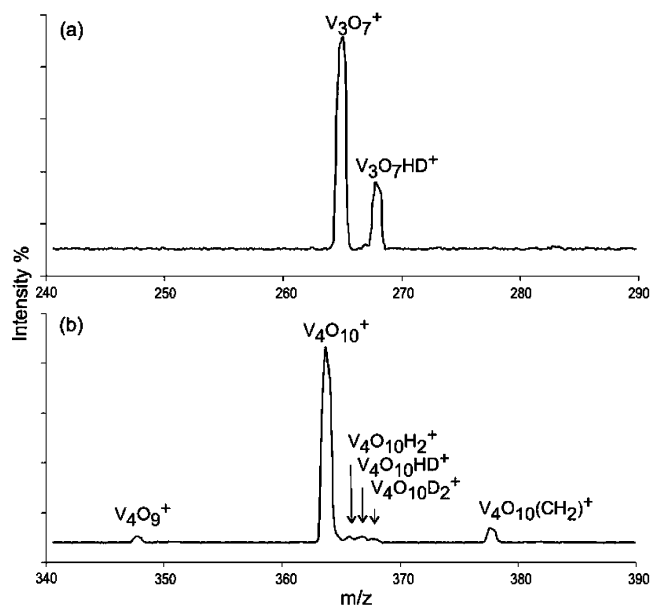


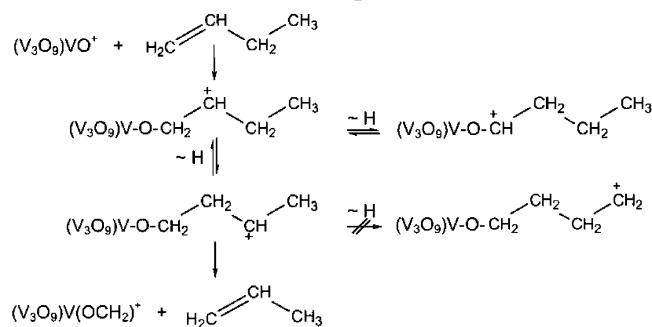
Figure 4. ODH of $CD_3CH_2CHCH_2$ (**1a**) by (a) $V_3O_7^+$ and (b) $V_4O_{10}^+$. $p(\mathbf{1a}) = 2.7 \times 10^{-4}$ mbar; collision energy adjusted to nominally 0 eV.

the formation of a $C_4H_8^+$ cation concomitant with loss of the corresponding neutral vanadium oxide ($V_mO_n^+ + C_4H_8 \rightarrow C_4H_8^+ + V_mO_n$). Hydride transfer results in production of the $C_4H_7^+$ cation concomitant with elimination of a neutral vanadium hydroxide ($V_mO_n^+ + C_4H_8 \rightarrow C_4H_7^+ + V_mO_nH$). The abundance of hydride transfer is comparable for both vanadium-oxide cations, whereas that for electron transfer initiated by $V_4O_{10}^+$ clearly dominates the electron transfer induced by $V_3O_7^+$ for all four isomers of butene. This result makes sense in that a d^0 radical like $V_4O_{10}^+$ can be expected to have a larger recombination energy than the closed-shell cation $V_3O_7^+$. Moreover, the ionization energies of isomeric butenes³³ are in agreement with the trend of 1-butene seeking less electron transfer than *cis*- and *trans*-butene. In addition, a minor signal is also detected at m/z 69 for the reactions of $V_3O_7^+$ and $V_4O_{10}^+$ with all four isomeric butenes which is assigned to $C_5H_9^+$ or $C_4H_5O^+$ but not investigated any further.³⁴

The reaction of $V_4O_{10}^+$ with 1-butene additionally leads to decreases of 14 and 16 mass units and an increase of 14 mass units (see Table 1, footnote *d*).³⁵ The observed gain of 14 mass units for 1-butene can be assigned to the product $[V_4O_9(OCH_2)]^+$ concomitant with a formal CH_2 transfer to the cluster; this process is most likely accompanied by hydrogen rearrangement prior to product release which we assign to the elimination of propene. Some mechanistic details are revealed by labeling experiments with **1a** and **1b**. Clean CH_2 transfer in the reaction with $CD_3CH_2CHCH_2$ (**1a**) rules out a participation of the hydrogen atoms of the terminal methyl group. On the other hand, the labeling experiment with $CH_3CH_2CHCD_2$ suggests partial H/D equilibration, as indicated by CHD and CD_2 transfers to the cluster in a ratio of 1:2.5. A signal for CH_2 transfer to $V_4O_{10}^+$ is either not existent at all or much too weak to be detected in the reaction with this labeled alkene. Clearly, while partial H/D equilibration occurs, the results demonstrate that the rearrangement of the H atoms does not involve the terminal methyl group of **1a**; rather, it is confined to the methylene units of the substrate. A plausible reaction mechanism is proposed in Scheme 3.

The decrease of 16 mass units to form $V_4O_9^+$ remains unchanged regardless of which isotopologue of 1-butene is used.

SCHEME 3: Proposal for CH₂ Transfer to a VO Unit of V₄O₁₀⁺ Concomitant with H-Atom Rearrangement Prior to the Elimination of Propene



While several alternatives are conceivable, for example, an O-atom transfer from V₄O₁₀⁺ to the neutral molecule, loss of water from the ODH1 product V₄O₁₀H₂⁺, or elimination of formaldehyde from the CH₂ transfer product [V₄O₉(OCH₂)⁺], the labeling experiments are only compatible with a formal transfer of an O atom to the alkene substrate.³⁶ The decrease of 14 mass units is assigned to V₄O₉H₂⁺ and is simply formed by subsequent ODH1 of isomeric butene by V₄O₉⁺.

Some disagreement evolves for the IMRs of V₃O₇⁺ with 1-butene, *cis*-butene, and *trans*-butene in comparison with the extensive work of Castleman and co-workers.^{9a,i} Upon IMR of V₃O₇⁺ with isomeric butenes, they reported in addition to the results discussed here the formation of V₃O₆⁺, V₃O₆H₂⁺, and V₃O₆C₄H₆⁺. Furthermore, according to Castleman, the electron transfer product C₄H₈⁺ and the hydride transfer product C₄H₇⁺ are generated as major products in the reaction of V₃O₇⁺ with butenes. While it is quite possible that the respective vanadium-oxide products are not detected in the present work due to the minor intensities of these signals, our experiment for the V₃O₇⁺/butene systems (butene = 1-butene, *cis*-butene, and *trans*-butene) definitively showed oxidative dehydrogenation as a major route. Furthermore, we observe molecular addition to the ODH product to form V₃O₇H₂(C₄H₈)⁺ as well as 2-fold molecular addition yielding V₃O₇(C₄H₈)₂⁺, respectively, which were not reported by Castleman et al. Among others, a feasible rationale for the different experimental finding might be due to the different types of cluster ion sources used. While Castleman et al. employed a Smalley-type laser-vaporization source, in our experiments, the ESI method was applied, and it is thus conceivable that different amounts of excited states or isomeric ions are produced to some extent.³⁷ While we cannot assess

the validity of this conjecture for the experiment conducted by Castleman et al., the reactivities of the V_{*m*}O_{*n*}D_{*o*}⁺ ions generated upon ESI were found to be insensitive to the exact conditions in the ion source, the cone voltage in particular. Moreover, the considerable amount of adduct formation in our experiments strongly supports that quasi-thermal ions are formed in our experiment. This conclusion is after all not too unexpected because, despite the energizing conditions in the cone region, the ions emerging from the source subsequently still undergo multiple collisions in the extraction to the ultrahigh vacuum of the multipole setup.

Alkanes. As described in the previous section, the cations V₂O₂⁺ and V₄O₁₀⁺ were found to be the most reactive ones investigated in the present study as far as DH and ODH of butenes are concerned, respectively. Accordingly, the question emerges whether this also holds true in the reactivity toward alkanes.

Ion–molecule reactions carried out with various small alkanes, like ethane, propane, *n*-butane, and *iso*-butane, show that *only* V₂O₂⁺ and V₄O₁₀⁺ among all examined vanadium-oxide and -hydroxide clusters are capable of activating saturated hydrocarbons concerning DH and ODH. Further, the main channel for V₄O₁₀⁺ corresponds to ODH1 concomitant with transferring two hydrogen atoms to the cluster to form the reduced cation [V₄O₁₀H₂]⁺ (Figure 5 serves as an example for the reaction with propane). In addition, some transfer of one hydrogen atom from the alkane to the cluster to form the reduced cation [V₄O₁₀H]⁺ is also observed. Furthermore, the spectrum of V₄O₁₀⁺ shows loss of 16 mass units; this process may correspond to O-atom transfer to the alkane to form the corresponding alkanol(s) or loss of water from the ODH product V₄O₁₀H₂⁺. Eventually, organic products are also formed, like charge transfer to produce the cationic alkane concomitant with neutral V₄O₁₀, and with hydride abstraction to result in the cationic alkyl product concomitant with neutral V₄O₁₀H (Scheme 4). For the butane isomers, the reaction resulted additionally in minor signals which are assigned to C₃H₅⁺, C₃H₆⁺, and C₃H₇⁺.

On the other hand, mass-selected V₂O₂⁺ was only capable of activating propane, *n*-butane, and *iso*-butane but showed no activation of ethane. The reaction of the low-valent vanadium-oxide V₂O₂⁺ yielded in V₂O₂(C_{*n*}H_{2*n*})⁺ concomitant with loss of dihydrogen, which was assigned to DH, and in molecular addition to form V₂O₂(C_{*n*}H_{2*n*+2})⁺.

The normalized intensities for the four alkanes studied are summarized in Table 2. The standard deviations are anomalously large, thus preventing a quantitative analysis in terms of

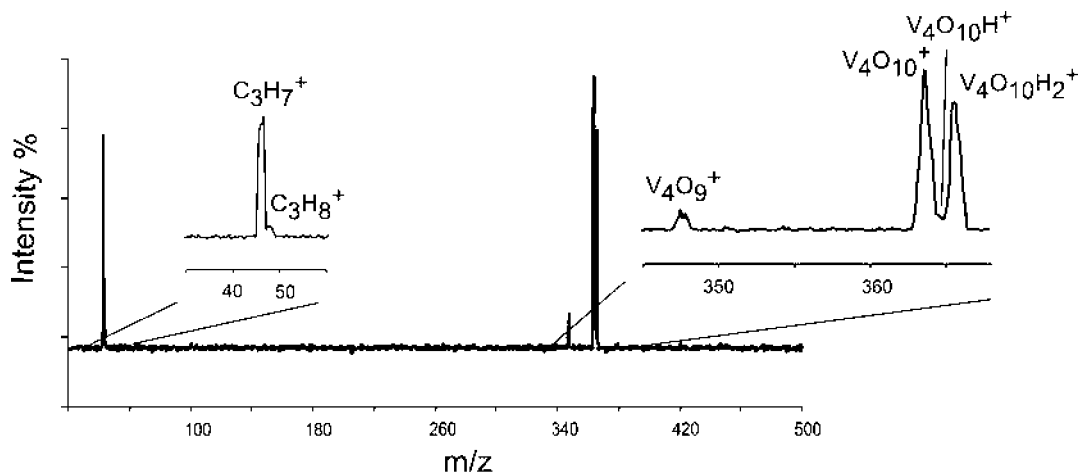
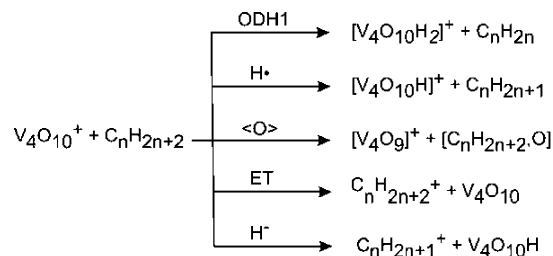


Figure 5. IMR of V₄O₁₀⁺ with propane. *p*(propane) = 2.7 × 10^{−4} mbar; collision energy adjusted to nominally 0 eV. The insets focus on the respective signals discussed in the text.

SCHEME 4: Primary Products for the Reactions of $V_4O_{10}^+$ with Alkanes (for Details, See Table 2)^a


^a The minor formations of $C_3H_5^+$, $C_3H_6^+$, and $C_3H_7^+$ for the reaction with isomeric butane are not included in the scheme.

TABLE 2: Averaged Branching Ratios for Product Channels in the Reactions of $V_4O_{10}^+$ with Small Alkanes^{a,b}

alkane	$V_4O_{10}^+$							$V_2O_2^+$	
	ODH1	H [•]	⟨O⟩	ET	H ⁻	$C_3H_7^+$	$C_3H_6^+$	$C_3H_5^+$	DH
<i>n</i> -butane	28	1	4	11	22	2	1	3	14
<i>iso</i> -butane	13	1	4	12	40	3	10	3	18
propane	32	5	6	4	34				8
ethane	42	16	10	0	5				

^a Experiments are carried out at equal pressures of alkanes, or the results are normalized. ^b The experimental error expressed as the standard deviation of the branching ratio is unusually large (up to ± 30); see text. Data are normalized to the most intense peak of the reactions with isomeric butenes.

reactivity trends. The large deviations may be caused by superposition of variable amounts of isobaric, but nonreactive isomers with reactive ones of the mass-selected precursor-ion beam in the particular case of $V_4O_{10}^+$ which is a minor signal upon ESI and further affected by “aging” of the precursor solution as described previously.¹⁹ An example for ion–molecule reaction of $V_4O_{10}^+$ with propane is shown in Figure 5.

Notwithstanding, the ionization energies of the alkanes agree well with the result that isomers of butane have the lowest ionization energy (IE) and show the highest abundance for electron transfer. In contrast, ethane with the highest IE does not lead to electron transfer at all. This trend applies for H abstraction as well, which has the highest abundance for *iso*-butane and the lowest for ethane.³³

Some further insight into the mechanism is achieved by isotope-tracer studies of $V_4O_{10}^+$ with, for example, 2,2-dideuteriopropane, $CH_3CD_2CH_3$ (**2**). ODH of isotopically labeled propane resulted in mass gains of 2, 3, and 4 mass units, which implies transfer of H_2 , HD, and D_2 , respectively. Consequently, an H/D equilibration is operative, and the intensities observed for the gains of H_2 /HD/ D_2 upon reaction with $V_4O_{10}^+$ correspond to a completely statistical distribution of the H and D atoms in the precursor molecule (statistical result for the incorporation of H_2 /HD/ D_2 = 53:43:4; experimental data: H_2 /HD/ D_2 = 53:44:3). The resulting apparent primary kinetic isotope effect of KIE = 1 indicates that in the transition structure the C–H(D) bond is either hardly or already almost completely cleaved.³⁸ Accordingly, the rate-determining step of the present reaction does not correspond to a C–H(D) bond activation of the alkane but may rather be associated with product or reactant formation as well as intracomplex electron transfer.^{39,40} The latter appears as a likely conjecture because electron transfer to $V_4O_{10}^+$ (recombination energy (RE) = 11.8 \pm 0.3 eV)⁴¹ delivers enough energy required for the ionization of propane (IE = 10.94 \pm 0.05 eV).⁴²

As described in the previous section, the labeling experiments with the labeled butenes **1a** and **1b** exhibited similar reactivities and reaction mechanisms for $V_2O_2^+$, $V_2O_4^+$, $V_2O_5^+$, and $V_4O_{10}^+$, and yet in the reactivities with alkanes $V_2O_2^+$ and $V_4O_{10}^+$ brings about bond activation. An explanation to this puzzle is found in a qualitative comparison of their ionization energies. In contrast to $V_4O_{10}^+$ (and $V_2O_2^+$), the cations $V_2O_4^+$ (RE = 8.2 eV) and $V_2O_5^+$ (RE = 9.8 eV) have recombination energies that are too low to ionize saturated hydrocarbons, such as ethane (IE = 11.52 \pm 0.04 eV), propane (IE = 10.94 \pm 0.05 eV), *n*-butane (IE = 10.53 \pm 0.02 eV), and *iso*-butane (IE = 10.68 \pm 0.11 eV).^{42–44} Likewise, the closed-shell cation $V_3O_7^+$, which shows the highest ODH activity toward isomeric butenes, is not capable of any dehydrogenation of alkanes, most likely due to a misfit of the RE/IE data.

Conclusions

Oxidative dehydrogenation (ODH) and dehydrogenation (DH) of isomeric butenes are observed for various vanadium-oxide and -hydroxide clusters, such as $V_2O_2^+$, $V_2O_4^+$, $V_3O_6^+$, $V_3O_7^+$, and $V_4O_{10}^+$. The reactivity trends for these two types of dehydrogenation reactions suggest that high-valent clusters prefer ODH concomitant with the addition of two hydrogen atoms to the cluster oxide cations and elimination of neutral butadiene. In contrast, the low-valent clusters tend to add the diene with parallel loss of molecular hydrogen (DH). For $V_2O_2^+$ and $V_4O_{10}^+$, the occurrence of H/D equilibration with the isotopically labeled 1-butenes $CD_3CH_2CHCH_2$ and $CH_3CH_2CHCD_2$ indicates a different reaction mechanism for these cations than that for the other reactive vanadium-oxide cluster cations investigated in the present study. Further, oxidative dehydrogenation of small alkanes is observed only for $V_4O_{10}^+$ and dehydrogenation only for $V_2O_2^+$. The difference in reactivity can be ascribed to the operation of a different reaction mechanism for $V_4O_{10}^+$, in which C–H bond activation of the alkane does not constitute the rate-determining step; quite likely, an intracomplex electron transfer mechanism is crucial, the occurrence of which is subject to a proper balance of the recombination/ionization energies of the two partners involved in the reactions.

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- (30) (a) The reaction of $V_2O_5^+$ with $CH_3CH_2CHCD_2$ (**1b**) has not been measured.
- (31) A slight electron and hydride transfer is also obtained for $V_4O_8^+$ (BR = <1%).
- (32) A minor signal was detected also at m/z 57 and is viewed as consecutive H transfer to the butene cation $C_4H_8^+$.
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- (34) Intensities: $V_3O_7^+$ (isomeric butenes), BR <1%; $V_4O_{10}^+$ (1-butene), 6; $V_4O_{10}^+$ (iso-butene), 4; $V_4O_{10}^+$ (cis-butene), 3; $V_4O_{10}^+$ (trans-butene), 1.
- (35) IMR of $V_4O_{10}^+$ with cis-butene only leads to very slight loss of oxygen (BR <1%).
- (36) Loss of one O atom from $V_4O_{10}^+$ may originate either from simple release of one atom to form $V_4O_9^+$ or from O-atom transfer to the alkene to form the corresponding oxygenated products. Branching ratios were measured for the loss of oxygen by collision experiments with argon, xenon, and alkenes under identical conditions. (Here, argon is also chosen as the target, as it has a similar mass as the alkanes employed.) The absence of the $V_4O_9^+$ fragment upon colliding $V_4O_{10}^+$ with either argon or xenon suggests oxygen transfer from the vanadium-oxide cation to the alkene.
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