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Dehydration and Dehydrogenation of Alcohols with Mononuclear Cationic Vanadium Oxides in the Gas Phase and Energetics of $VO_nH^{0/+}$ ($n = 2, 3$)

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Dedicated to Professor Peter Hofmann on the occasion of his 60th birthday

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The ion/molecule reactions of selected alcohols with the vanadium oxide cations VO^+ and VO_2^+ are studied by Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometry. Dehydrogenation is the dominating reaction pathway for methanol and allyl alcohols. With larger or less unsaturated alcohols, dehydration and carbocation formations prevail. While the valence in VO^+ remains unchanged during alcohol dehydrogenation, VO_2^+ is reduced to V^{III}. Thermochemical data for $VO_2H^{0/+}$, VO_3H and $VO_3H_2^+$ are derived by means of ICR bracketing. The experimental results are further complemented by ab initio calculations using density functional theory.

Introduction

Part of the large interest in transition-metal oxides is due to their key role in heterogeneous catalysis,[1] particularly in oxidation reactions. For example, vanadium oxide compounds are used as heterogeneous catalysts[2] for the oxidation of SO_2 in the production of sulfuric acid and for selective hydrocarbon oxidation, i.e. the production of maleic anhydride directly from butane. The mechanisms of such complicated hydrocarbon activations are still not fully understood and widely debated.[1] Among others, alcohols and alkoxides have been proposed as intermediates in alkane oxidation catalyzed by metal-oxide compounds.[1–3] Further, the oxidation of alcohols itself is important for industrial processes, e.g. the production of formaldehyde from methanol.[1,4] For larger molecules containing alcoholic OH groups, acidic properties of an oxide catalyst may induce dehydration instead of dehydrogenation.[1,2] Hence, a selective oxidation catalyst is characterized by handling the delicate interplay between oxidizing and acidic properties. The roles of formal oxidation states and of functional groups that form the active sites of a catalyst are of particular interest in this respect.

Gas-phase experiments represent a powerful means for conducting model studies of complicated reactions,[5,6] ranging even to models for heterogeneous catalysis,[7] because they facilitate an understanding of mechanistic details at a molecular level. It has to be stated though that the extreme simplification also entails that a direct extrapolation of the findings to applied catalysis may be impossible.[8] The gas-phase behavior of vanadium alkoxides have been studied for methanol[9,10] and larger homologues.[11] As far as detailed studies are concerned, only methanol dehydrogenation by vanadium cations has been previously addressed.[12–14] Here, we present an experimental investigation of the gas-phase ion/molecule reactions of the mononuclear vanadium-oxide cations VO^+ and VO_2^+ with a variety of alcohols. The results have some implications for the ion thermochemistry of the vanadium-oxide hydroxides VO_2H and VO_3H, which has not been reported so far.

Results

Ion/Molecule Reactions of VO^+ with Selected Alcohols

In the comparatively sluggish reaction of VO^+ with methanol, the major process corresponds to dehydrogenation, which has been shown to proceed via a selective 1,2-elimination.[13] In contrast, dehydrogenation is an only minor pathway in the reaction of VO^+ with ethanol (Table 1). The longer carbon chain enables a new reaction pathway (alkene formation) which is also reflected in an enhanced overall reaction efficiency (ϕ = 35%).[15] Use of the labeled reactant [2,2,2-D_3]ethanol leads to an exclusive loss of $C_2H_2D_2$. Thus, ethene formation takes place via a selective 1,2-elimination. The cationic product $[VO_2H_2]^+$ may be both the water complex $VO(H_2O)^+$ or the more

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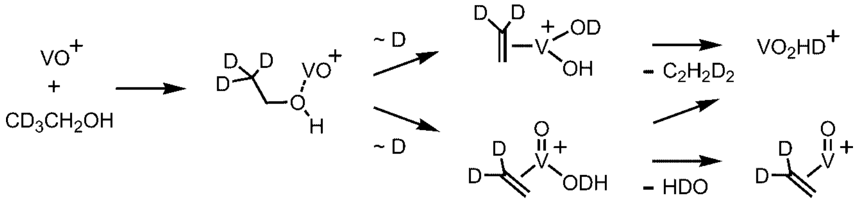
Table 1. Experimental second-order rate constants (k), reaction efficiencies (ϕ)[15] and primary neutral products[a] for the ion/molecule reactions of VO^+ with alcohols.

	CH_3OH[b]	C_2H_5OH	n-C_3H_7OH	iso-C_3H_7OH	n-C_4H_9OH	sec-C_4H_9OH	CH_2CHCH_2OH	$CH_3CHCHCH_2OH$	$CH_2CHCHOHCH_3$	$CH_2CHCH_2CH_2OH$
k[c]	1.2	6.7	7.3	6.4	9.1	8.6	9.6	7.0	8.2	5.3
ϕ [%]	6	35	40	35	50	50	50	40	45	30
H_2	95	20	5	4	[d]	[d]	32	1	3	2
2 H_2			3	2	1	2		1	1	2
CH_4	5		1	1						1
CH_4, H_2					8	4				
H_2O		2	1	3			6	13	20	15
H_2, H_2O					22	10		3	5	4
C_2H_4		77				1	5	6	9	10
C_2H_6					10	40				
C_3H_4							7			
C_3H_6			75	77	1					17
C_4H_6								30	32	22
C_4H_8					52	38				
CH_2O							5			8
VO_2H			15	13	6	5	28	45	30	19
C_3H_5							17			

[a] Intensities are normalized to a sum of 100%. For all systems, fragmentation channels with abundances ≤ 1% are neglected. [b] Taken from ref.[13] [c] Given in 10^{-10} cm^3 $molecule^{-1}$ s^{-1}; the absolute error is assumed to be ± 30%. [d] This ion is formed in a quick and efficient secondary reaction, which may contribute to the primary branching ratio with max. 2%.

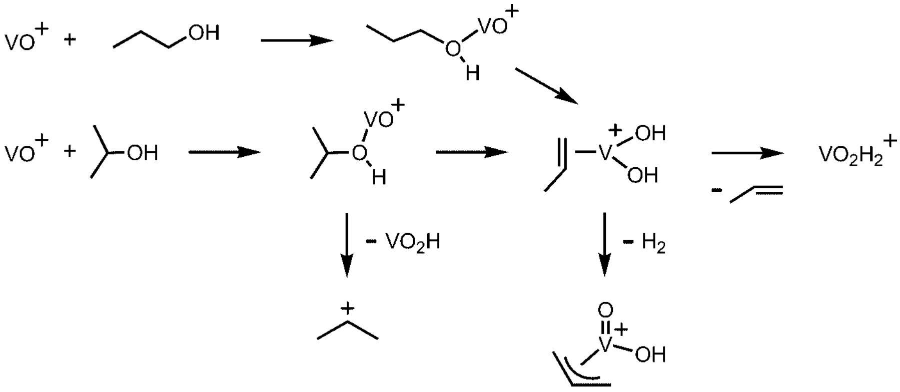


Scheme 1.

stable dihydroxide $V(OH)_2^+$.[16,17] In competition with ethene loss, water is expelled in a much smaller amount, and as far as site-selectivity is concerned, investigation of [2,2,2-D_3]ethanol demonstrates high selectivity (Scheme 1). Both reaction pathways result in a dehydration of ethanol to ethene, even though the bisligated complex $VO(C_2H_4)(H_2O)^+$ does not necessarily need to serve as a common intermediate in both cases.[18]

Most of the fragmentation pathways in the ion/molecule reaction of VO^+ with propanol (Table 1) resemble the ethanol case, i.e. elimination of propene concomitant with formation of $VO_2H_2^+$ represents the most abundant reaction channel and dehydrogenation takes place in even lower amounts. The latter yields the ion $[VC_3H_6O_2]^+$, which has been previously characterized as the allyl complex (C_3H_5)-$VO(OH)^+$.[19] Further, formation of the carbocation $C_3H_7^+$ appears as a new pathway which is not observed for the smaller alcohols (Scheme 2). The nature of the neutral species $[VO_2H]$ lost in this process cannot be probed in our type of experiments. Nevertheless, it is reasonable to interpret it as a vanadium-oxide hydroxide O=V–OH, because combined elimination of VO and $HO^\cdot$ is endothermic ($\Delta_r H$ = 415 kJ/mol for 2-propanol) and hence for this channel impossible in ion/molecule reactions with thermalized reactants. The overall oxidation state of vanadium therefore does not change during this reaction which can be viewed as a transfer of a hydroxide anion from the alcohol to the metal cation. Even though the hydroxy group is situated at different positions in the two propanol isomers, the spectra of 1- and 2-propanol are indistinguishable (Table 1). Starting from 1-propanol, a direct hydroxide transfer would lead to an energetically demanding primary carbocation. On the other hand, an additional hydrogen rearrangement in the positively polarized hydrocarbon ligand yields the more stable secondary carbocation which is formed directly in the 2-propanol case and can thus account for the experimental observations.

Similar to propanol, the reactions of VO^+ with isomeric butanols predominantly result in the formation of $VO_2H_2^+$ concomitant with loss of butene. In addition, hydroxide abstraction, yielding $C_4H_9^+$ is also observed. No significant differences between the two butanol isomers are observed, again indicating the formation of a secondary carbocation in both cases. As a new reaction channel, a combined elimination of H_2O and H_2 takes place, which leads to $[VC_4H_6O]^+$. Tentatively, this product ion is assigned to the complex $VO(C_4H_6)^+$ with 1,3-butadiene as a bidentate ligand.[19] In addition, some C=C bond cleaving channels are observed, which do not take place for the smaller alcohols. Among these, the formation of $[VC_2H_4O_2]^+$ via loss of ethane or C_2H_4 + H_2 is especially noteworthy because it is strongly enhanced for *sec*-butyl alcohol compared to 1-butanol. The pronounced difference demonstrates that the position of the hydroxy group is crucial for this kind of C–C bond cleavage and that OH abstraction should not be involved.



Scheme 2.

Allyl alcohol is also dehydrated by VO^+, but dehydrogenation and OH-transfer give rise to the dominating reaction channels. In analogy to the methanol case, the cationic dehydrogenation product is tentatively assigned to the acrolein complex $VO(CH_2CHCHO)^+$. Further, losses of ethene and $[CH_2O]$ are detected in small amounts, the latter may be formaldehyde or, less probable, a consecutive expulsion of CO after dehydrogenation. Interestingly, OH-abstraction does not only lead to the allyl cation $C_3H_5^+$ and neutral VO_2H, but also to the alternative couple of products with the opposite charge distribution $VO_2H^+ + C_3H_5^{\cdot}$: note that this the only case in the present investigation in which the cationic species VO_2H^+ was observed (see below).

Finally, the reactions of VO^+ with isomeric butenoles result in the main fragmentation channels expected according to the preceding results: Dehydration leads to both $VO(C_4H_6)^+$ and $VO_2H_2^+$, whereas hydroxide transfer results in $C_4H_7^+$. Note that VO_2H^+ is not observed reflecting the lower ionization energy of $C_4H_7^{\cdot}$ compared to $C_3H_5^{\cdot}$ (7.9 eV vs. 8.18 eV).[20] Further, small amounts of ethene loss are detected which may correspond to the expulsion of $[C_2H_6]$ as observed for the butanols. With regard to the three butenol isomers studied here, the differences between the two allylic alcohols are mostly confined to relatively small variations of abundances, whereas two additional products are observed for $CH_2CHCH_2CH_2OH$; these correspond to the eliminations of propene and $[CH_2O]$, respectively. The latter processes resemble the expulsions of ethene as well as $[CH_2O]$ from allyl alcohol/VO^+ (see above).

In summary, the main pathway in the reactions of VO^+ with alcohols is dehydration. Both alkenes and water may be expelled as neutral products, but alkene loss is far more favored. Dehydrogenation to aldehyde or ketone complexes is also possible, but can only compete efficiently if alkene formation cannot take place (methanol) or if the substrate already is too unsaturated (allyl alcohol). As a third important reaction pathway, hydroxide abstraction by VO^+ is observed. The C_4-alcohols further undergo cracking processes in which C–C bonds are cleaved. In any case, the metal's oxidation state (V^{III}) remains unchanged in the products formed.

Ion/Molecule Reactions of VO_2^+ with Selected Alcohols

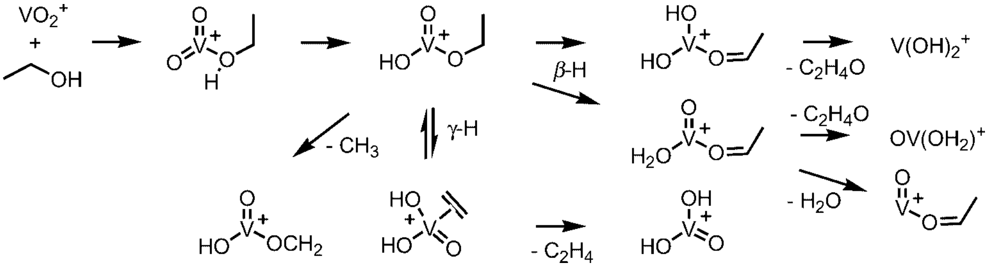
When reacted with bare VO_2^+, methanol is converted to formaldehyde with $VO(CH_2O)^+$ and $VO_2H_2^+$ as the corresponding ionic products.[13] In contrast to the VO^+ case, the reaction can be termed as an oxidative dehydrogenation, i.e. water is formed instead of H_2, while the metal is reduced from V^V to V^{III}. In the reaction of VO_2^+ with ethanol (Table 2), oxidative dehydrogenation is expressed in the losses of H_2O and $[C_2H_4O]$. The latter is tentatively assigned to acetaldehyde. Yet, the enhancement in reaction rate (ϕ = 50% as compared to ϕ = 10% for the VO_2^+/CH_3OH system) is attributed to ethene formation representing the by far most abundant reaction channel. This scenario resembles very much the behavior of VO^+ described above. The product ion $VO_3H_2^+$ may be interpreted as doubly protonated vanadate VO_3^-. In solution, condensation to polyvanadates takes place upon acidification of vanadate solutions.[21] In the gas phase, however, any oligomerization is strictly prevented by the real Coulomb charge of the ions. Therefore, stable protonated monomeric species such as $VO_3H_2^+$ are feasible as well. A reaction pathway unique to the ethanol/VO_2^+ system leads to $[VCH_3O_2]^+$ via methyl loss. Whereas expulsion of $CH_3^{\cdot}$ has also been reported for the reaction of FeO^+ with ethanol,[22] a similar process has not been observed so far in any ion/molecule reaction of vanadium oxides with alcohols or hydrocarbons.[19] Formation of an open-shell fragment results in a reduction of V^V in VO_2^+ to V^{IV} in the product ion. A reasonable structure is $OV(OH)(CH_2O)^+$ formed by methyl loss from the putative ethoxy intermediate $OVOH(OC_2H_5)^+$ (Scheme 3). However, the reaction with [2,2,2-D_3]ethanol demonstrates that partial H/D exchange precedes all reaction pathways depicted in Scheme 3. As a possible candidate for an intermediate in the H/D equilibration one may consider the structure $VO(OH)_2(C_2H_4)^+$ with two identical hydroxy and methylene groups.

The ion/molecule reactions of VO_2^+ with 1- and 2-propanol do not show any significant differences. Similar to dehydration of ethanol by VO^+, formation of $VO_3H_2^+$ concomitant with elimination of propene is a prominent reaction

Table 2. Experimental second-order rate constants (k), reaction efficiencies (ϕ),[15] and primary neutral products[a] for the ion/molecule reactions of VO_2^+ with alcohols.

	CH_3OH[b]	C_2H_5OH	n-C_3H_7OH	iso-C_3H_7OH	n-C_4H_9OH	sec-C_4H_9OH	CH_2CHCH_2OH	$CH_3CHCHCH_2OH$	$CH_2CHCHOHCH_3$	$CH_2CHCH_2CH_2OH$
k[c]	2.0	9.0	10.5	9.4	7.6	8.4	6.9	7.9	9.6	7.8
ϕ [%]	10	50	60	55	45	50	40	45	55	45
CH_3		3								
H_2O	28	5		1	1					
H_2, H_2O			4	3	1	5				
CH_2O	72						5			
C_2H_6						10				
C_2H_4		76								
C_3H_4							10			
C_3H_6			38	37						5
C_3H_8					8					
C_2H_4O		10						1	3	
$[C_2H_6O]$					8	7				
C_4H_6								4	7	1
C_3H_4O							10			
C_4H_8					20	18				
C_3H_6O			4	2		4				
C_4H_8O					7	10				
$[C_2H_6O_2]$		4								
$[C_4H_{10}O_2]$					5	4				
VO_3H			54	53	39	33	75	93	85	90
$[VC_2H_5O_2]$									3	

[a] Intensities are normalized to a sum of 100%. For all systems, fragmentation channels with abundances ≤ 2% not listed. Note that the nature of the lost neutral molecule is not known, and that the mass difference may correspond to two (or more) smaller molecules. [b] Taken from ref.[13] [c] Given in 10^{-10} cm^3 molecule^{-1} s^{-1}; the absolute error is assumed to be ± 30%.



Scheme 3.

pathway. The major route is associated with hydroxide abstraction to afford neutral VO_3H. The facile formation of a carbenium ion may also account for the lack of differentiation between 1- and 2-propanol.

In the reactions with isomeric butanols, butene formation and hydroxide abstraction represent the main reaction pathways. However, they are not as favored as in the propanol cases. In addition, a manifold of minor and almost negligible reaction channels is observed as well, which we do not pursue in any further detail.[23] Further, several types of C–C bond cleavages take place, some of which exhibit significant differences between n-butyl and sec-butyl alcohol. For example, sec-butyl alcohol/VO_2^+ shows loss of C_2H_6, whereas C_3H_8 is expelled in the case of 1-butanol. Thus, the position of the OH group has a significant effect on the cracking processes both in the reactions of VO^+ and VO_2^+.

The spectra of ion/molecule reactions of VO_2^+ with unsaturated alcohols are comparatively simple (Table 2). With allyl alcohol, the formations of $C_3H_5^+$ as the major and VO^+, $VO_2H_2^+$, $VO_3H_2^+$ as minor primary products are observed in analogy to the results described above. The reaction of VO_2^+ with butenol isomers finally reveals a pronounced preference for carbocation formation; only traces of other reaction channels are observed.

In summary, the two most favored pathways in the alcohol/VO_2^+ systems, alkene expulsion and carbocation formation, both include C–O bond cleavage of the alcohol. Hydroxide transfer takes place if the resulting carbenium ion is sufficiently stabilized. Labeling experiments suggest that the two pathways are connected by tautomerism between alkene and hydroxide complexes before dissociation. With unsaturated alcohols, hydroxide abstraction is observed almost exclusively in accordance with the enhanced stability of allyl cations.

Secondary Ion/Molecule Reactions in the Alcohol/VO^+ and Alcohol/VO_2^+ Systems

Cascades of the subsequent ion/molecule reactions of VO_n^+ cations with methanol have previously been studied in detail.[13] The key reactions steps comprise condensation reactions of the type [V]OH + CH_3OH → [V]OCH_3 + H_2O, where [V] stands for a bare or ligated, neutral or charged vanadium core. A similar behavior is observed for other alcohols ROH as well, for which ions of the formula $V(OH)(OR)^+$ and $V(OR)_2^+$ are formed from $VO_2H_2^+$ and the respective alcohol. On the other hand, isomeric complexes $VO(ROH)^+$ may be present too. They stem from other intermediates and are formed via ligand exchange according to $VO(L)^+ + ROH \rightarrow VO(ROH)^+ + L$ (L = CH_3CHO, for example), even though they should be significantly less stable than the alkoxide isomers.[13] Further, the presence of complexes of the type $OVOH(R)^+$ as a third class of isomers is quite reasonable for larger alcohols which form more stable carbenium ions.[19] $VO_3H_4^+$ is another common product observed at longer reaction times with alcohols larger than methanol. This ion is produced via alcohol dehydration/alkene loss from the precursor ion $VO_2H_2^+$. Similarly, $VO_4H_4^+$ is formed from $VO_3H_2^+$; condensation leads to $VO(OH)(OR)^+$ and $VO(OR)_2^+$ in this case. If a carbocation is generated in the first step, it readily reacts with alcohol molecules in acid-base type reactions, yielding protonated alcohols and a typical series of organic cations derived there from. In addition to these more general observations, the reaction of VO^+ with the isomeric butanols shows a peculiarity in that the expected alkoxide product $[VC_4H_{10}O_2]^+$ is less abundant than the dehydrogenated ion $[VC_4H_8O_2]^+$. The latter may be assigned to a mixture of a butadiene complex $V(OH)_2(C_4H_6)^+$ and an unsaturated alkoxide $HOVC_4H_7^+$ formed via remote functionalization,[24] because a similar product is not observed for smaller alcohols.

Finally, the reactivity of the product VO_2H^+, generated from allyl alcohol/VO^+, was explored with regard to possible thermochemical implications. In the reaction of VO_2H^+ with allyl alcohol, mostly $C_3H_5^+$ concomitant with neutral $[VO_3H_2]$ are formed via a second hydroxide abstraction. Additional minor products correspond to $VO_2H_2^+$, $VO_3H_3^+$, $[C_3H_5O]^+$, and $[VC_3H_7O_3]^+$. The hydrogen-atom abstraction to yield a hydroxy-substituted allyl cation will again be addressed in the thermochemical section further below (Table 3).

Fragmentation of VO(alcohol)$^+$ Complexes in a Sector-Field Instrument

To gain further insight into the reaction mechanisms, an alternative instrumental technique has been used to study some of the postulated intermediates. To this end, the complexes VO(alcohol)$^+$ were attempted to be generated by chemical ionization of a mixture of $(C_5H_5)V(CO)_3$ and the respective alcohol with N_2O as reagent gas. The cations emerging from the CI source were then analyzed in a four-sector instrument by recording metastable ion spectra. By this technique, the charged fragments formed via unimolecular dissociations in the field-free region of the mass spectrometer are detected.

In the presence of methanol, a signal at *m/z* 99, as expected for $VO(CH_3OH)^+$, can be generated under CI conditions. The MI spectrum of the mass-selected ion shows H_2-loss as the main fragmentation channel (Table 3) with VO^+ and VO_2^+ as additional ionic fragments. All pathways are in accordance with previous findings[9] and the results obtained in ion/molecule reaction of VO^+ with methanol (see above). The exclusive loss of HD from CD_3OH/VO^+ confirms once more the operation of a selective 1,2-elimination. Similarly, selecting the ion at *m/z* 113 observed in the presence of ethanol leads to the observation of the same ions as in the respective ICR ion/molecule reaction. However, the relative abundances of the fragmentation channels differ significantly: dehydrogenation is now much more pronounced than dehydration, which can in part be associated with the conservation of angular momentum which leads to a preference for the losses of light fragments in the metastable ion spectra.[25,26] Further, the loss of 28 u shifts to 32 u when perdeuterated [D$_6$]ethanol is used, thus corroborating the formation of $VO_2H_2^+$ and neutral ethene. Elimination of H_2 remains the main fragmentation channel also for the two isomeric propanol complexes; minor losses of water or propene are observed as well. A difference between the two propanol isomers occurs with respect to the abundance of

Table 3. MI mass spectra of selected VO(alcohol)$^+$ or isomeric complexes.[a]

		CH_3OH[b]	CD_3OH[b]	CH_3CH_2OH	CD_3CD_2OD	*n*-C_3H_7OH	*iso*-C_3H_7OH	CH_2CHCH_2OH
$[M^+ - 1]$	H					2		5
$[M^+ - 2]$	H_2	100		100		100	100	100
$[M^+ - 3]$	HD		100					
	H_2 + H					4		
$[M^+ - 4]$	D_2		15		100			
$[M^+ - 16]$	CH_4	50						
$[M^+ - 18]$	H_2O			15		20	20	55
$[M^+ - 19]$	CD_3H		30					
	$[H_3O]$					15	4	3
$[M^+ - 20]$	D_2O				15			
$[M^+ - 28]$	C_2H_4, CO			85		25		5
$[M^+ - 32]$	CH_3OH, C_2D_4	25			70			
$[M^+ - 35]$	CD_3OH		25					
$[M^+ - 40]$	C_3H_4							5
$[M^+ - 42]$	C_3H_6					15	65	
$[M^+ - 52]$	CD_3CD_2OD			[b]	15			

[a] Intensities are normalized to the base peak (100); errors are assumed to be $< 10\%$. [b] The overall abundances in the methanol and ethanol systems were rather low such that signals with $I < 15$ could not be detected.

propene expulsion, which is significantly enhanced for 2-propanol. Interestingly, the formation of $C_3H_7^+$ via loss of neutral VO_2H, as observed in the corresponding ion/molecule reactions, is not observed in the MI-spectra. In addition, two other fragment ions corresponding to losses 19 u and 28 u, respectively, are observed. Whereas the latter is assigned to C_2H_4 because it is only detected for 1-propanol, but not for 2-propanol,[27] with regard to the former we cannot strictly exclude an isobaric interference in the MI experiments. Finally, the MI spectra obtained for the VO^+ complex of allyl alcohol display dehydrogenation as the most abundant process, but also significant amounts of water are lost. Instead of the loss of CH_2O observed in the ICR measurements, cleavage of atomic $H^{\cdot}$ is found. In conclusion, the sector experiments are consistent with the other data obtained, but at least for this particular system their information content remains somewhat limited due to the relatively weak signal abundances, caused by the lack of a suitable precursor for high yields of reasonably clean VO^+ ions.

Discussion

Ion/Molecule Reactions of VO^+ and VO_2^+ with Alcohols

Comparison of the observed reactions of VO^+ with those of VO_2^+ reveals similarities as well as some differences. Intuitively, similarities are expected for the reaction channels in which the cations act like Lewis acids, i.e. hydroxide abstraction and dehydration, whereas differences should appear in oxidation reactions like dehydrogenation, because V^V compounds (VO_2^+) are stronger oxidizing agents than V^{III}-species (VO^+). The reaction efficiencies do not differ significantly. In contrast to the reactions of VO^+ and VO_2^+ with alkanes,[19] the reactivity towards alcohols is not enhanced significantly by the second oxygen atom in VO_2^+. This behavior is in agreement with a Lewis-acid type interaction of the metal with the OH-group dominating the reactions of the two cations with alcohols larger than methanol, whereas the C–H bond activation necessary for alkane dehydrogenation is affected by the oxidation state of the metal.

The most important reaction channel in the methanol/VO^+ system is the formation of a formaldehyde complex by elimination of H_2. In the respective reaction with VO_2^+, two complementary fragmentation channels involve oxidation of methanol to CH_2O, i.e. loss of water and loss of CH_2O. As already stated above, oxidative dehydrogenation instead of pure dehydrogenation occurs with VO_2^+ instead of VO^+. In the VO^+ system, formaldehyde is not expelled, most probably because the hypothetical cationic product $HVOH^+$ is not as stable as the observed complex $VO(CH_2O)^+$. In contrast, $V(OH)_2^+$ is a likely product when the system contains an additional oxygen atom. A similar reasoning applies for the ethanol case simply by replacing an α-H atom by a methyl group. Still, oxidative dehydrogenation is less favored than dehydration to ethene for both vanadium-oxide cations. The discrimination of H_2-loss is even stronger with larger alcohols. From propanol on, the possible generation of stabilized secondary carbocations enables hydroxide abstraction from the substrate. The latter is more pronounced than dehydration only with VO_2^+, but not with VO^+, indicating that the proton affinity of VO_2H is lower than the one of VO_3H. Similarly, in the reactions with allyl alcohol, carbocation formation is significantly more pronounced with VO_2^+ than with VO^+. Further, the reverse charge distribution is only observed with VO^+, but not with VO_2^+. Therefore, the ionization energy of VO_3H must be significantly larger than $IE(C_3H_5^{\cdot})$ and thus $IE(VO_2H)$, in accordance with the more general observation of increasing ionization energies of vanadium-oxide species with increasing oxygen content.[28]

Comparison with Ion/Molecule Reactions of Other Cationic Transition-Metal Oxides

The reactions of FeO^+ with alcohols may be chosen for comparison with a typical late transition-metal oxide.[22,29] As compared to the behavior of FeO^+, the selectivity of VO^+ is markedly enhanced. Thus, losses of radicals are not observed at all for the latter, and a cleavage of propanol C–C bonds does not occur either in the ion/molecule reactions of VO^+. Further, carbocation formation does not occur for primary alcohols and FeO^+, whereas rearrangement to the more stable secondary carbocation obviously takes place in the alcohol/VO^+ systems. The main products in the reactions of FeO^+ with alcohols have been divided into three categories: α-oxidation, alkene loss, and carbocation formation. The same classification can be applied for the VO^+ reactions as well, but the channels follow rather different reaction mechanisms. For example, α-oxidation with FeO^+ leads to loss of H_2O, whereas H_2 is formed in the VO^+ reaction. This behavior reflects the significantly larger oxophilicity of the early transition metal vanadium in comparison to the late transition metal iron.[8] With respect to alcohol dehydrogenation, FeO^+ resembles more the vanadium dioxide VO_2^+ rather than the monoxide VO^+, as has already been predicted from similar M–O bond dissociation energies in FeO^+ and VO_2^+.[8]

In addition, the ion/molecule reactions of MoO^+ with alcohols have been reported.[30] Not surprisingly, the similarities to VO^+ are much more pronounced here. Thus, the strong M–O bond is never cleaved for both VO^+ and MoO^+. Nevertheless, some deviations still are detectable. For example, a selective α-oxidation of methanol occurs for both metal oxides. However, H_2 is lost as a neutral molecule in the case of VO^+, whereas CH_2O is expelled with MoO^+. Similarly, dehydration of ethanol to ethene takes place with both metal oxides, but water instead of ethene is lost with MoO^+. Finally, MoO^+ does not show any cracking products with butanols, again in contrast to the reactions of VO^+. In summary, VO^+ only effectively dehydrogenates alcohols if dehydration cannot compete, whereas dehydrogenation is always a good choice for MoO^+. Further, loss of oxygen-containing neutral molecules like aldehydes or water takes place with MoO^+, but is almost prohibited for VO^+.

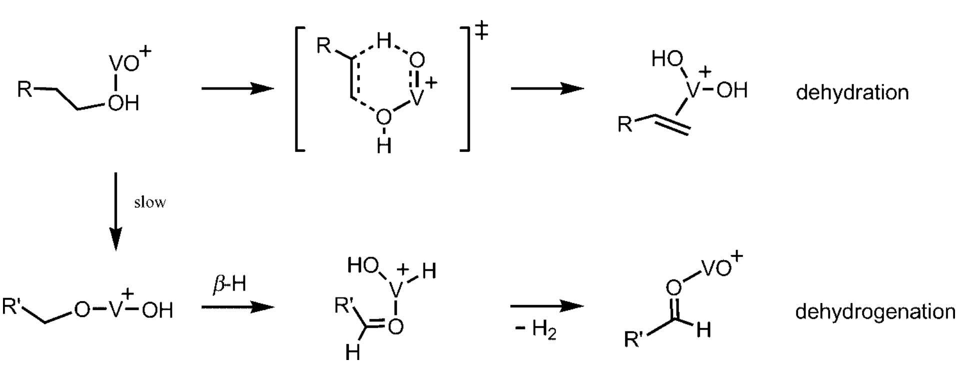
Comparison of ICR and Sector-Field Results

According to the elemental composition, the same ions are sampled in the ICR- and MI-spectra described above. Nevertheless, quite large deviations in relative intensities are observed which cannot be explained only by mass discrimination effects known to enhance losses of small neutral molecules in sector instruments[31] and effects of angular momentum.[25,26] As another likely reason for the differences we therefore propose different ion internal energies in both experiments. In general, unimolecular fragmentation channels of metastable ions generated under CI conditions are less energy-demanding than fragmentations of the corresponding encounter complexes formed in ion/molecule reactions under single-collision conditions.[32] In the alcohol/VO^+ systems discussed here, the main difference concerns the enhanced amount of dehydrogenation instead of dehydration as observed in the MI spectra. According to DFT calculations of *n*-propanol/VO^+, dehydrogenation indeed is the lowest exit channel.[19] The strong preference for the energetically slightly more demanding dehydration of propanol in the ICR experiments might be due to spin restrictions,[33] such an argumentation has been proposed for the related system propane/VO_2^+.[19] However, spin restrictions cannot explain the similar results observed for ethanol, because both dehydrogenation and dehydration occur only on one (triplet) spin state in this case. Nevertheless, dehydrogenation again is preferred in the MI spectra, whereas dehydration to $VO_2H_2^+$ prevails under ICR conditions. As an alternative, rearrangements taking place during the formation and stabilization of the ions by collisions in the CI source should be taken into account. In our case, isomerization from an alcohol complex $VO(ROH)^+$ to the more stable alkoxide $V(OH)(OR)^+$ is likely to happen and should even be catalyzed by collisions with alcohol molecules.[17,34] Some indications for the presence of an alkoxide structure can be found in the CA spectra which show signals at *m*/*z* 68 (VOH^+) and *m*/*z* 84 (VO_2H^+) in addition to the one at *m*/*z* 67 (VO^+). Formation of these ions in high-energy collisions is more likely from $V(OH)(OR)^+$ isomers than from $VO(ROH)^+$. In conclusion, the observed MI spectra might stem from a mixture of two non-interconverting isomers. With the assumption that the ICR branching ratios roughly represent the fragmentations of the alcohol complexes $VO(ROH)^+$, the differences to the MI spectra can be ascribed to the alkoxides $V(OH)(OR)^+$. Thus, the alcohol complex mostly yields alkene formation, whereas H_2-loss is preferred for the alkoxide. The different reactivities can be understood as follows. In the alcohol complex, the C–OH bond is weakened to some extent due to coordination to the Lewis-acidic metal oxide cation. It is even broken completely for allyl alcohol resulting in a complex $(C_3H_5)V(O)(OH)^+$. Dehydration of the alcohol to an alkene is then easily accomplished by transfer of a hydrogen atom from the hydrocarbon backbone to the vanadyl oxygen which may proceed directly via a six-membered transition structure (Scheme 4). In contrast, the isomeric alkoxide could undergo a *β*-H elimination to initiate hydrogen elimination leading to aldehyde or ketone complexes, respectively. For example, formaldehyde expulsion is observed upon dissociation of gaseous $OV(OCH_3)_3^+$ and several of its fragment ions.[9] Thus, the assumption of a mixture of isomers can explain the observed results reasonably well (Table 4).

Table 4. Heats of formation (in kJ mol^{-1})[a] of species used in the data analysis.

	Δ_fH		Δ_fH
H	218.0[b]	OH^-	138.9[k]
O	249.2 ± 0.1[c]	$C_2H_5^+$	902 ± 4[k]
OH	39.3 ± 0.2[d]	C_2H_5OH	-234.8 ± 0.2[k]
V^+	1162 ± 8[c]	$C_2H_5OH_2^+$	507[k]
VO	134 ± 12[e]	$C_3H_5^\cdot$	161[k]
VO^+	832 ± 12[f]	C_3H_5OH	-123.6 ± 1.5[k]
VOH^+	768 ± 15[g]	*sec*-$C_3H_7^+$	801 ± 4[b]
VO_2	-201 ± 55[h]	*iso*-C_3H_7OH	-272.5 ± 0.4[k]
VO_2^+	716 ± 16[i]	$CH_2CHC^\cdot HOH$	15.4[l]
$V(OH)_2^+$	372 ± 40[j]	CH_3CCH	185.4 ± 0.9[b]

[a] Values for gaseous species at 298 K. [b] Ref.[20] [c] Ref.[49] [d] Ref.[50] [e] Derived using *IE*(VO) = 7.2386 eV.[51] [f] Derived using $D_0(V^+–O) = 5.99 \pm 0.1$ eV.[52] [g] Derived using $D_0(V^+–OH) = 4.50 \pm 0.15$ eV.[52] [h] Derived using $IE(VO_2) = 9.5 \pm 0.4$ eV.[42] [i] Ref.[13] [j] Estimated using $\Delta_fH(V(OH)_2^+) = \Delta_fH(V^+) + 2\,\Delta_fH(OH) - 2\,D_0(V^+–OH)$. [k] Ref.[53] [l] Ref.[54]



Scheme 4.

Thermochemical Implications

For several of the molecules mentioned above, no thermochemical data have been reported so far, i.e. the hydroxide-oxides $VO_2H^{0/+}$, VO_3H and $VO_3H_2^+$. Accordingly, we summarize the thermochemical information which can be derived from the ICR experiments in which endothermic reactions cannot take place ("bracketing approach").

Neutral VO_2H cannot be observed directly by mass spectrometric means. Nevertheless, its formation can be deduced from carbocation observation in the reactions of VO^+ with alcohols. As already mentioned above, the alternative of generating two neutral molecules ($VO + OH^\cdot$) can be excluded due to its endothermicity. Therefore, carbocation formation can be used to derive upper limits for the enthalpy of formation $\Delta_f H(VO_2H)$. The lowest upper boundary $\Delta_f H(VO_2H) \leq -242 \pm 16\ kJ\,mol^{-1}$ results from the reaction VO^+ + 2-propanol → *sec*-$C_3H_7^+ + VO_2H$. An estimate of a lower limit may be calculated from the non-occurrence of a similar process in the ethanol case: $\Delta_f H(VO_2H) \geq -305 \pm 16$ kJ/mol. The corresponding cation VO_2H^+ is formed from VO^+ and allyl alcohol: $VO^+ + C_2H_3CH_2OH \rightarrow C_3H_5^\cdot + VO_2H^+$, thus yielding $\Delta_f H(VO_2H^+) \leq 547 \pm 20\ kJ\,mol^{-1}$. For a lower boundary, the subsequent reactions of VO_2H^+ with allyl alcohol are examined. However, the heat of formation of at least one product is not known for all reaction pathways. In the H-atom abstraction $VO_2H^+ + C_2H_3CH_2OH \rightarrow VO_2H_2^+ + [C_3H_5O]$, the formation of the radical $CH_2CHC^\cdot HOH$ may be assumed. Combined with an estimate for the enthalpy of formation $\Delta_f H(V(OH)_2^+)$ (Table 4), this leads to a lower bound of $\Delta_f H(VO_2H^+) \geq 511 \pm 40\ kJ\,mol^{-1}$. A comparison of the two bracketed values gives an estimate for the ionization energy $IE(VO_2H) = 8.3 \pm 0.2$ eV. This ionization energy can also be deduced directly. In the allyl alcohol/VO^+ system, the product channels $C_3H_5^+ + VO_2H$ and $VO_2H^+ + C_3H_5^\cdot$ are observed in a ratio of about 2:1, thus indicating $IE(VO_2H) \approx IE(C_3H_5^\cdot) = 8.18$ eV.[20] This result is further confirmed by the formation of $C_4H_7^+$ from but-3-en-2-ol/VO^+, whereas VO_2H^+ is not formed at all in this case, thus $IE(VO_2H) > IE(C_4H_7^\cdot) = 7.49$ eV.[20] On the other hand, hydroxide abstraction is not observed in the reaction of VO^+ with phenol,[35] which might be interpreted as an indication for $IE(VO_2H) < IE(C_6H_5^\cdot) = 8.32$ eV.[20]

In addition, DFT calculations on neutral and cationic $V(O)(OH)^{0/+}$ have been performed (Table 5). Previous benchmark calculations[9,36,37] have shown that the chosen level is convenient for a sufficiently accurate comparison with experimental results on mononuclear vanadium-oxide compounds, even though further calculations at highest ab initio levels are still desirable. The results obtained for the fragments fully confirm geometries and energetics reported previously.[19,36–40] The geometry of cationic $V(O)(OH)^+$ in the energetically most favorable doublet spin state ($^2A''$) meets the expectations: The V–O bond length (d_{VO} = 1.55 Å) is typical for cationic vanadyl units and the V–OH bond length fits to previous calculations of related compounds.[12] Compared to the cation, the V–O bonds in neutral V(O)(OH) with a triplet ground state ($^3A''$) are elongated. The calculated adiabatic ionization energy $IE_{calc}(V(O)(OH)) = 8.22$ eV is in perfect agreement with the experimental value $IE_{exp}(V(O)(OH)) = 8.18$ eV derived above. Comparison of the experimental and calculated bond energies (Table 6) further shows that the theoretical level is sufficiently high because the deviations are in acceptable ranges.

Table 5. Total energies E_{tot} (in Hartree) and selected geometric parameters[a] of neutral and cationic V(O)(OH) and some fragments calculated with B3LYP/TZVP.

		E_{tot}	d_{VO}[b]	d_{OH}	a_{OVO}	a_{VOH}
V(O)(OH)	$^3A''$	–1095.151804	1.61; 1.85	0.96	153.7	157.1
	$^1A'$	–1095.115031	1.60; 1.84	0.96	147.7	151.2
	$^5A''$	–1095.073974	1.79; 1.90	0.96	170.0	170.0
$V(O)(OH)^+$	$^2A''$	–1094.849715	1.55; 1.74	0.97	120.7	141.8
	$^4A'$	–1094.772115	1.72; 1.80	0.97	153.0	165.3
VO_2	$^2A_1$	–1094.523949	1.62		115.0	
VO_2^+	$^1A_1$	–1094.195535	1.56		105.9	
VO	$^4\Sigma^-$	–1019.237027	1.59			
VO^+	$^3\Sigma^-$	–1018.964283	1.55			
VOH	$^5A'$	–1019.818921	1.85	0.96		129.2
	$^1A'$	–1019.759570	1.72	0.96		179.9
	$^3A'$	–1019.740494	1.77	0.96		140.1
VOH^+	$^4A''$	–1019.580107	1.73	0.97		155.5
OH	$^2\Pi$	–75.757786		0.98		
O	^3P	–75.095258				
H	^2S	–0.502154				

[a] Bond lengths *d* [Å] and bond angles *a* [°]. [b] The first value given corresponds to the vanadyl V=O bond, the second to the V–O single bond.

Table 6. Comparison of some selected calculated and experimental bond dissociation energies for $VO_2H_n^{0/+}$ (n = 0–2) in $kJ\,mol^{-1}$.

X–Y	$D(X–Y)_{calc}$	$D(X–Y)_{exp}$
OV^+–O	357	365 ± 20[a]
OV–O	503	585 ± 60[a]
OV^+–OH	335	340 ± 40[b]
OV–OH	412	450 ± 40[b]
OVO^+–H	399	405 ± 40[b]
OVO–H	330	290 ± 40[b]

[a] Derived from the data in Table 4. [b] This work.

In conclusion, the bond dissociation energy D(OVO–H) = $290 \pm 40\ kJ\,mol^{-1}$ in neutral VO_2H reflects a weak O–H bond, whereas the OV–OH bond is rather strong (D(OV–OH) = $450 \pm 40\ kJ\,mol^{-1}$). Ionization of V(O)(OH) to $V(O)(OH)^+$ requires $IE_{exp}(OVOH) = 8.18$ eV and leads to a decrease in V–OH bond strength $D(OV^+–OH) = 340 \pm 40\ kJ\,mol^{-1}$, whereas the strength of the VO–H bond rises to $D(OVO^+–H) = 405 \pm 40\ kJ\,mol^{-1}$, which is significantly more than $D(VO^+–H) = 282 \pm 15\ kJ\,mol^{-1}$ in VOH^+.

Very similar to the VO_2H case, reasonable boundaries for the enthalpy of formation of neutral VO_3H can be obtained from its formation in the reaction of VO_2^+ with 2-propanol ($\Delta_f H(VO_3H) \leq -358 \pm 16\ kJ\,mol^{-1}$) and its non-occurrence in the reaction with ethanol ($\Delta_f H(VO_3H) \geq -421 \pm 16\ kJ\,mol^{-1}$). For the corresponding protonated species $VO_3H_2^+$, the upper limit $\Delta_f H(VO_3H_2^+) \leq 407 \pm 17\ kJ\,mol^{-1}$ is based on the reaction VO_2^+ +

$C_2H_3CH_2OH \rightarrow VO_3H_2^+$ + propyne. As stated above, formation of protonated alcohols is one of the major subsequent products in the alcohol/VO_2^+ systems. Thus, the reaction $VO_3H_2^+ + C_2H_5OH \rightarrow VO_3H + C_2H_5OH_2^+$ may be used to derive $\Delta_fH(VO_3H_2^+) \geq 350 \pm 50$ kJ mol^{-1}. Note that this limit might be too high because the intermediate $VO_3H_2^+$ has not been thermalized.

In the reactions of VO_2^+ with alcohols, formation of both product channels $VO_3H_2^+$ + alkene and VO_3H + alkyl$^+$ takes place. The relative carbocation abundance I_{rel} correlates with the proton affinity of the hydrocarbon involved (Figure 1). This is an indication for the presence of a tautomer equilibrium before dissociation, i.e. $[C_mH_n^+\cdot VO_3H]$ and $[C_mH_{n-1}\cdot VO_3H_2^+]$. The former complex can arise by direct hydroxide transfer from the alcohol to VO_2^+. The existence of the latter has already been proposed in the discussion (Scheme 3) due to partial H/D exchange observed during the reaction. A similar mechanistic scenario has been described earlier for the reactions of FeO^+ with alcohols.[22] According to Figure 1, the proton affinity $PA(VO_3H)$ lies between $PA(C_2H_4)$ = 680 kJ mol^{-1} and $PA(C_4H_6)$ = 783 kJ mol^{-1}, because for ethanol the equilibrium is shifted completely on the side of $VO_3H_2^+$ and mostly to the carbocation side for the isomeric butenols. $I_{rel} = 0.5$ is expected for a proton affinity slightly lower than the one of propene, thus leading to $PA(VO_3H) = 730 \pm 10$ kJ mol^{-1}. Note that $I_{rel} = I(C_3H_5^+)/(I(VO_3H_2^+) + I(C_3H_5^+)) = 0.88$ for the reaction of allyl alcohol with VO_2^+ suggests that the hydroxide abstraction is not followed by a rearrangement of allene to the thermochemically more stable propyne,[20] because the amount of $VO_3H_2^+$ is significantly lower than in the butanol systems even though the proton affinities of propyne and *trans*-butene are similar. Combination of $\Delta_fH(VO_3H) = -390 \pm 50$ kJ mol^{-1} and $PA(VO_3H) = 730 \pm 10$ kJ mol^{-1} leads to $\Delta_fH(VO_3H_2^+) = 410 \pm 60$ kJ mol^{-1}, which compares reasonably well with the lower boundary derived above.

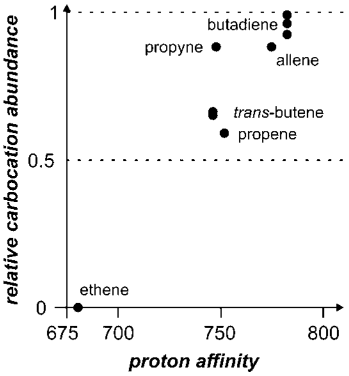


Figure 1. Relative carbocation abundance $I_{rel} = I$(carbocation)/[I(carbocation) + $I(VO_3H_2^+)$] vs. proton affinities[20] (in kJ mol^{-1}) of the produced alkenes in the reactions of VO_2^+ with alcohols.

The different branching ratios for the reactions of VO_2^+ and VO^+ with alcohols cannot be explained by the stability of the carbocations formed because they are the same in both cases. But one may assume that the difference in selectivity might be due to an enhanced exothermicity of the charge recombination reaction $VO_2^+ + OH^- \rightarrow VO_3H$ compared to the similar formation of VO_2H from VO^+ which could also lower the corresponding transition structure. However, the formation of neutral VO_3H from $VO_2^+ + OH^-$ ($\Delta_rH = -1245$ kJ mol^{-1}) is not favored compared to $VO^+ + OH^- \rightarrow VO_2H$ ($\Delta_rH = -1246$ kJ mol^{-1}) according to the data derived here. Thus, the different bond dissociation energies simply reflect the different ionization energies of VO and VO_2.

Conclusions

Due to the Lewis-acidic character of vanadium-oxide cations, dehydration prevails in their ion/molecule reactions with most alcohols investigated. Oxidation of the alcohol can only compete efficiently for methanol and allyl alcohol, for which dehydration is unfavorable. The monoxide VO^+ mediates dehydrogenation without changing the metal's oxidation state (V^{III}). The reaction with VO_2^+ (V^V) leads to the very same product ions. The metal therefore is reduced and water instead of hydrogen is formed. Thus, VO_2^+ induces an oxidative dehydrogenation of alcohols. During the major pathways of larger alcohols with VO_2^+, a pre-equilibrium between alkene and hydroxide complexes is proposed as the relative amount of carbocation vs. alkene formation clearly reflects the respective proton affinities. In contrast to the fragmentation behavior of the alcohol complexes $VO(ROH)^+$, the metastable ion spectra of the isomeric alkoxides $V(OH)(OR)^+$ reveal a preference for dehydrogenation even for alcohols larger than methanol.

Experimental Section and Computational Details

Ion/molecule reactions were examined with a Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source as described elsewhere.[32,41] In brief, V^+ is generated by laser ablation of a vanadium target using a Nd:YAG laser operating at 1064 nm. A series of potentials and ion lenses is used to transfer the ions into the ICR cell, which is positioned in the bore of a 7.05 T superconducting magnet. Mass-selected $^{51}V^+$ is then converted to VO^+ or VO_2^+ by reaction with pulsed-in O_2 or N_2O, respectively.[17,42] During the gas pulses, the ions undergo several hundreds of collisions such that the product ions are assumed to be thermalized.[43] The reactivity of the mass-selected ion of interest was studied by introducing neutral reactants via leak valves at stationary pressures in the order of 10^{-8} mbar. The experimental second-order rate constants are evaluated assuming the pseudo first-order kinetic approximation after calibration of the measured pressures and acknowledgement of the ion gauge sensitivities;[44] the error of the absolute rate constants is assumed to be ± 30%, while the error for the relative rate constants is only 10%.

Additional experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described in detail previously.[45] Briefly, cations were generated by chemical ionization (CI) of mixture of $(C_5H_5)V(CO)_4$ and the respective alcohol using N_2O as reagent gas. After acceleration to a kinetic energy of 8 keV, the ions were mass-selected and subjected to metastable ion (MI) and collisional activation (CA) studies. MI spectra of B(1)/E(1) mass-selected ions were recorded by detection of the charged fragments formed unimolecularly in the field-free region between E(1) and B(2) by scanning the latter sector. CA spectra were recorded in the same manner using helium (80% transmission) as a stationary collision gas. As the CA spectra were all dominated by the MI signals, only the MI spectra are discussed here. Nevertheless, the CA spectra confirm that the selected ion really is a vanadium-oxide species as indicated by the presence of signals for V^+, VO^+, VOH^+, $VO_2{}^+$, VO_2H^+ or $VO_2H_2{}^+$. The error of the reported abundances amounts up to 10% due to low yields in the gas-phase synthesis of the desired complexes.

All unlabeled reagents and $(C_5H_5)V(CO)_4$ were used as purchased and introduced by conventional vacuum techniques. The labeled alcohols were synthesized following well-known laboratory procedures.[27]

All calculations employed the hybrid density-functional theory (DFT) B3LYP method[46] implemented in the Gaussian 98 program package[47] in combination with Ahlrichs' valence triple-ζ basis sets with polarization functions on all atoms[48] which yielded good results in a previous benchmark study of vanadium alkoxides.[9] Vibrational frequencies were computed for all stationary points obtained in order to confirm that each optimized geometry corresponds to a local minimum. All energies given below refer to 0 K and include zero-point energy correction.

Acknowledgments

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