

Fragmentation of Alkoxo(catecholato)vanadium(v) Complexes $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$ in the Gas Phase

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Keywords: Alkoxo complexes / Catecholates / Elimination / Hydrogen migration / Vanadium

Electrospray ionization (ESI) mass spectrometry is used to investigate the gas-phase dissociation behavior of vanadium(v) complexes $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$ containing two identical or different alkoxy groups ($R^1, R^2 = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7$ and $t-C_4H_9$) and a catecholato ligand ($C_6H_4O_2$). The fragmentation reactions of the complexes are studied by collision-induced dissociation (CID) and labeling experiments. For $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$ cations with alkoxo groups

larger than methyl, a trend for preferential evaporation of hydrocarbon fragments is observed, followed by expulsion of neutral alcohols. Further, the CID spectra of all complexes show a signal which can be assigned to the complex $[(C_6H_4O_2)VO]^+$.

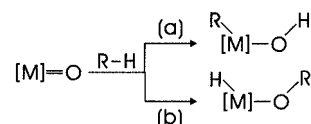
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Introduction

Over the past years, interest in transition-metal oxides has grown steadily, due to the promising role which these compounds play in heterogeneous catalysis.^[1] Metal oxides often serve as catalysts which are characterized by high selectivities and activities in many processes.^[2] An important group of transition-metal catalysts are vanadium oxides,^[3] used, for example, in the oxidation of sulfur dioxide in the industrial production of sulfuric acid and for the oxidation of hydrocarbons, e.g. propane and *n*-butane, to valuable products such as maleic acid and its anhydride. With respect to the oxidation of saturated hydrocarbons, mixed vanadium oxide/vanadium phosphate oxide (VPO) is of particular interest as a catalyst.^[4]

Interest in transition-metal alkoxides arises from their potential role in metal-mediated oxidation reactions. High-valent transition-metal oxo complexes have been recognized to enable activations of C–H or O–H bonds in many important chemical and biological processes.^[5] In general, C–H bond activation of alkanes by a transition-metal oxide $[M]=O$ can occur in two different ways (Scheme 1). The first conceivable route (a) is transfer of a hydrogen atom from a C–H bond to the oxygen atom concomitant with bonding of the alkyl residue to the metal atom. The alternative reaction (b) involves C–O bond formation which yields a metal alkoxide concomitant with an additional metal–hydrogen bond.

For many reactions of transition-metal oxides with alkanes it is not easy to predict a clear preference for one of these routes. Experimental data needed for such a prediction are often not available because many of the relevant



Scheme 1.

species are either difficult to isolate or elusive. Theoretical approaches are an attractive alternative under these circumstances, although application of quantum mechanical calculations to coordinatively unsaturated transition-metal compounds is all but trivial. In particular, many reactions of transition-metal oxides involve many low-lying excited electronic states.^[6–9] Theoretical investigations of the activation of methane by the bare metal oxide cation FeO^+ , which serves as a prototype for C–H bond activation of alkanes by transition-metal oxides in the gas phase,^[6,10] predict preference of reaction (a), but route (b) is also not too energy-demanding and is conceivable as well.^[11] Further, the formation of alkoxometal complexes has been proposed in the reactions of oxides of group V–VIII transition metals with methanol.^[12] Metal alkoxides are also important intermediates in the dihydroxylation of olefins by OsO_4 ,^[13] and reactions of the chromium dioxide cation with hydrocarbons in the gas phase.^[14] With respect to our particular interest in vanadium alkoxides, the presence of $VOCH_3$ units has been considered essential for the selective oxidation of methanol to formaldehyde.^[15,16]

In this article, we present an experimental study of composite vanadium(v) cations in the gas phase, which contain two identical or different alkoxy groups. The interest is focused on the examination of the effects of the substituents on the dissociation behavior of the complexes. More simple vanadium complexes like trimethylvanadate have been suc-

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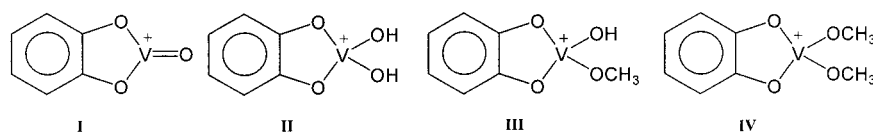
cessfully examined before by various spectrometric means.^[17] For our investigation, we aimed at producing vanadium(v) complexes of the type $[(L)V(OR^1)(OR^2)]^+$ in the gas phase, where R^1 , $R^2 = CH_3$, C_2H_5 , $n-C_3H_7$, $i-C_3H_7$, and $t-C_4H_9$. Our first choice for the ligand L to which the vanadium atom is connected by two single bonds through oxygen atoms was $[(C_2H_4O_2)V(OR^1)(OR^2)]^+$, where $C_2H_4O_2$ corresponds to glycolate. In this case, however, the fragmentations were not unequivocal, because several of the fragment ions observed can be assigned to dissociation of alkoxy groups as well as to the dissociation of the glycolate unit. Therefore, we switched to the more robust catechol ligand, for which such a problem does not exist (see below). Our focus lies on alkoxovanadium(v) complexes, which might be formed as transient intermediates in the oxidation of alkanes by vanadium oxides, because low-valent vanadium oxide cations and clusters cannot oxidize alkanes.^[18–21]

In the experiments, electrospray ionization (ESI) mass spectrometry is employed, a technique which permits transfer of ionic complexes into the gas phase directly from solution, with a variable degree of desolvation or fragmentation. The possibility of analyzing the complexes in the gas phase in the absence of solvent provides essential information about ion structures and stoichiometries. Understanding of the gas-phase chemistry of transition-metal alkoxides can therefore provide insight into their fundamental properties at a molecular level and might thereby help to explain their behavior in the condensed phase.

Results

ESI of $VOCl_3$, dissolved in different alcohols and mixtures of alcohols with a small amount of catechol, leads to the formation of the desired vanadium(v) complexes $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$. The abundances of the ions of interest critically depend on the concentration of catechol as well as the mixing ratio of the alcohols. If the concentration of catechol in the solution is too high, complexes with a $[(C_6H_4O_2)V(C_6H_4O_2)]^+$ core prevail. Likewise, the yields of the mixed alkoxy complexes are poor, when the concentration of the second alcohol is too small, as formation of $[(C_6H_4O_2)V(OR^1)_2]^+$ prevails.

In the cation ESI spectra of $VOCl_3$ in methanol with catechol under soft ionization conditions, the monocationic vanadium(v) complexes shown in Scheme 2 are observed. In structure **I**, the metal center V^V is connected with the aromatic ring through the oxygen atoms of catechol and forms an additional double bond with the vanadyl oxygen atom. This cation appears in the mass spectra of all mixtures examined.



Scheme 2.

The CID spectrum of mass-selected **I** ($m/z = 175$) shows a mass difference of $\Delta m = -28$ (Table 1), which may be assigned to expulsion of CO or C_2H_4 ; given the $VC_6H_4O_3^+$ stoichiometry of **I**, loss of C_2H_4 appears unlikely, however. By analogy, $\Delta m = -44$ is assigned to loss of CO_2 . The CID spectra of **I** recorded at higher collision energies are dominated by VO^+ with additional signals corresponding to $\Delta m = -28$, -44 , -56 , and -72 , which can be assigned to CO, CO_2 , two molecules of CO, and possibly $CO + CO_2$, respectively. For the cation **II** ($m/z = 193$), containing two hydroxy groups, the main process upon CID is loss of a water molecule ($\Delta m = -18$), which formally leads to **I**. Likewise the strong signal for $\Delta m = -32$ evolving in the case of complex **III** ($m/z = 207$) can be assigned to the loss of methanol. Similar to cation **III**, the CID spectra of complex **IV** containing two methoxy groups bound to a vanadium(v) center are characterized by the elimination of methanol ($\Delta m = -32$), which can be explained by the mechanism depicted in Scheme 3. The key step corresponds to a hydrogen migration from the carbon atom of one to the oxygen atom of the second methoxy group. This scenario also accounts for the experimentally observed loss of formaldehyde ($\Delta m = -30$). The CID spectrum is dominated, however, by the expulsion of a CH_3 radical ($\Delta m = -15$), a process which is unique for the complex with $R^1 = R^2 = CH_3$; the fragment with $\Delta m = -45$ is assigned to a combined loss of $CH_3 + CH_2O$. The CID spectra of mass-selected $[(C_6H_4O_2)V(OCD_3)_2]^+$ fully confirm these conclusions in that preferential eliminations of CD_3 ($\Delta m = -18$), CD_2O ($\Delta m = -32$), and CD_3OD ($\Delta m = -36$) are observed.

Table 1. Neutral losses (given as mass differences, Δm) observed upon CID of the mass-selected cations **I–IV**, generated by ESI of $VOCl_3$ with catechol in methanol. Data given relative to the base peak (100) of the CID products at $E_{lab} = 3$ eV.

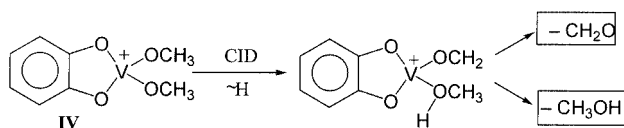
	-15	-18	-28	-30	-32	-44	-45
I			100			60	
II		100	96				
III					100		
IV	100			55	45		27

The CID spectra of the mixed methoxy complexes $[(C_6H_4O_2)V(OCH_3)(OC_2H_5)]^+$, $[(C_6H_4O_2)V(OCH_3)(OC_3H_7)]^+$ and $[(C_6H_4O_2)V(OCH_3)\{OC(CH_3)_3\}]^+$ are dominated by losses of corresponding alkenes generated from the larger alkoxy group, i.e. C_2H_4 , C_3H_6 , and C_4H_8 , respectively (Table 2). Alkene elimination leads to the formation of **III**, prior to further degradation to structure **I** (Scheme 4). Minor dissociation pathways correspond to the expulsion of alcohols: methanol and ethanol from $[(C_6H_4O_2)V(OCH_3)(OC_2H_5)]^+$, methanol and propanol for the $[(C_6H_4O_2)V(OCH_3)(OC_3H_7)]^+$ complex, and finally,

Table 2. Neutral losses observed upon CID (collision gas: xenon) of mass-selected $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$ complexes generated by ESI of $VOCl_3$ with $C_6H_4(OH)_2$ in methanol, ethanol, *n*-propanol, isopropyl alcohol, *tert*-butyl alcohol, and in mixtures of these alcohols. Data given relative to the base peak (100) of the CID products at $E_{lab} = 3$ eV.

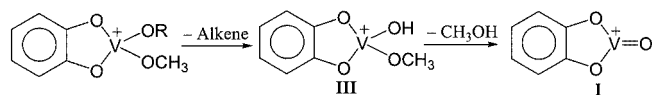
R^1/R^2	-15	-18	-28	-30	-32	-42	-46	-56	-60	-74	-84	-88	-98	(c)/(d) ^[a]
CH_3/CH_3 ^[b]	100			65	37									100:0
CH_3/C_2H_5			100		15		14		11					21:79
$CH_3/n-C_3H_7$					6	100			11	7				14:86
$CH_3/i-C_3H_7$					100	62			77	15				70:30
$CH_3/t-C_4H_9$		44			19			100		13		13		22:78
C_2H_5/C_2H_5			100				80	30		3				37:63
$C_2H_5/n-C_3H_7$			1			100	15		6					17:83
$C_2H_5/i-C_3H_7$						100	78		33					53:47
$C_2H_5/t-C_4H_9$							33	100		7				28:72
$n-C_3H_7/n-C_3H_7$						100			1		70			1:99
$n-C_3H_7/t-C_4H_9$						6		100					3	3:97
$i-C_3H_7/i-C_3H_7$						100			<5 ^[c]		75			<3:>97
$i-C_3H_7/t-C_4H_9$						1		100	22				3	21:79
$t-C_4H_9/t-C_4H_9$								100		32				24:76

[a] Ratio of hydrogen transfer according to routes (c) and (d), see Scheme 6 and text for details. [b] In addition, a consecutive loss of CH_3 and CH_2O is observed (Δm (%) = -45 (30)). [c] Poor abundances of $[M^+]$ formed upon ESI; the value given is an upper limit derived from the noise level.



Scheme 3.

methanol and *tert*-butyl alcohol for the cation- $[(C_6H_4O_2)V(OCH_3)(OC(CH_3)_3)]^+$, respectively. For the latter complex, also loss of water is observed ($\Delta m = -18$). The CID spectra of mass-selected $[(C_6H_4O_2)V(OCH_3)(OCH_2CD_3)]^+$ generated from [2,2,2- D_3]ethanol reveal a preferential combined elimination of $C_2H_2D_2$ ($\Delta m = -30$) and CH_3OD ($\Delta m = -63$). The labeling experiments thereby confirm that the key reactions under CID of mixed methoxy complexes correspond to losses of alkenes according to Scheme 4.

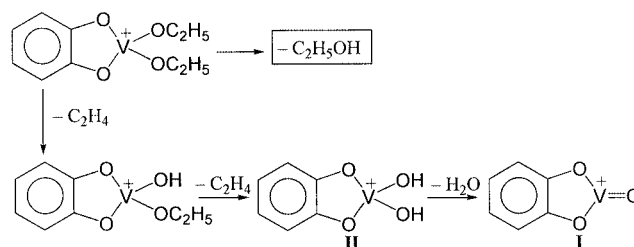


Scheme 4.

The CID spectra of mass-selected $[(C_6H_4O_2)V(OCH_3)\{OCH(CH_3)_2\}]^+$ are also characterized by the elimination of C_3H_6 , but the reaction does not dominate in this case. Instead, the major fragmentation is associated with an expulsion of methanol ($\Delta m = -32$), along with smaller amounts of $(CH_3)_2CHOH$ ($\Delta m = 60$).

Similar to the complexes containing one methoxy group and another larger alkoxy group, expulsion of ethene ($\Delta m = -28$) predominates upon CID of mass-selected $[(C_6H_4O_2)V(OC_2H_5)_2]^+$; expulsion of ethanol is observed also ($\Delta m = -46$). Possible pathways for the neutral losses upon CID of $[(C_6H_4O_2)V(OC_2H_5)_2]^+$ are presented in Scheme 5, which also suggest the formation of **II** by a consecutive loss of a second C_2H_4 unit followed by the elimination of H_2O to finally yield **I**. Note that the route via **II** is impossible for the complexes with a methoxy ligand as

shown in Scheme 4, because alkene elimination is not feasible for $R = CH_3$. Upon CID of mass-selected $[(C_6H_4O_2)V(OC_2H_5)(OC_2D_5)]^+$, eliminations of C_2H_4 ($\Delta m = -28$) and C_2D_4 ($\Delta m = -32$) compete with each other with an apparent kinetic isotope effect (KIE) of 2.3 ± 0.1 associated with H-migration from the β -carbon atom in the course of alkene elimination. The significant magnitude of the KIE implies that C-H bond activation is rate-determining, as expected.^[22,23]



Scheme 5.

The CID spectra of mixed complexes containing one ethoxy group are dominated by expulsion of alkenes from the larger alkoxy group: C_3H_6 for $[(C_6H_4O_2)V(OC_2H_5)(OC_3H_7)]^+$ as well as $[(C_6H_4O_2)V(OC_2H_5)\{OCH(CH_3)_2\}]^+$ cations and C_4H_8 for $[(C_6H_4O_2)V(OC_2H_5)\{OC(CH_3)_3\}]^+$, respectively, along with smaller amounts of corresponding alcohols (Table 2).

The fragmentations of $[(C_6H_4O_2)V(OC_3H_7)_2]^+$ and $[(C_6H_4O_2)V\{OCH(CH_3)_2\}]^+$ are very similar to each other. In both cases, the major CID signal corresponds to the loss of C_3H_6 ($\Delta m = -42$). As a result, cations containing one hydroxy group $[(C_6H_4O_2)V(OH)(OC_3H_7)]^+$ and $[(C_6H_4O_2)V(OH)\{OCH(CH_3)_2\}]^+$ are formed. These ions undergo a second loss of C_3H_6 ($\Delta m = -84$) to yield structure **II**, which can then expel water to finally afford **I**. Likewise, the CID spectra of $[(C_6H_4O_2)V(OC_3H_7)\{OC(CH_3)_3\}]^+$ and $[(C_6H_4O_2)V\{OCH(CH_3)_2\}\{OC(CH_3)_3\}]^+$ are quite similar and characterized by the elimination of C_4H_8 fragments

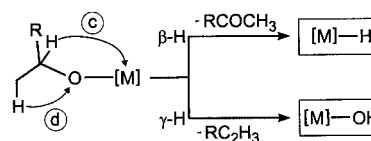
($m/z = 235$) along with small amounts of neutral *tert*-butyl alcohol. For $[(C_6H_4O_2)V(OC_3H_7)\{OC(CH_3)_3\}]^+$ an additional signal is present at $m/z = 249$, which can be assigned to the expulsion of C_3H_6 (Table 2). The fragmentation of the vanadium(v) complex with two *tert*-butoxy groups under CID conditions leads to predominant formation of the $[(C_6H_4O_2)V\{OC(CH_3)_3\}(OH)]^+$ concomitant with neutral butene. Also in this case, formation of complex **I** is observed at elevated collision energies.

Discussion

The comparison of the CID patterns of the various alkoxovanadium(v) complexes described above allows some general trends in reactivity to be derived. As a first and obvious conclusion, the dimethoxy complex $[(C_6H_4O_2)V(OCH_3)_2]^+$ is considered as being unique in that it cannot undergo olefin loss and instead expels a methyl radical which is only observed for this particular complex. Formally, the expulsion of $CH_3^\cdot$ affords a free valence at the remaining oxygen atom, thus formally leading to a hypervalent vanadium compound or an oxygen-centered radical. However, catechol can be considered to act as a redox-active ligand^[24] in that electronic rearrangement may lead to an $OV(OCH_3)^+$ cation coordinated to an *ortho*-quinone ligand, i.e. a formal vanadium(IV) complex. For the other complexes, a clear trend for the preferential evaporation of hydrocarbon fragments from the larger alkoxy group is observed, followed by evaporation of neutral alcohol ligands (R^1OH and R^2OH).

In recursion to the above results, it is interesting to consider the fragmentation processes occurring upon CID in terms of one of two possible routes. Quite obviously, the trends among the various alkoxovanadium cations depend on the structure of the alkoxy groups. For a more detailed consideration, some kind of categorization of the reactions observed is required. Let us therefore distinguish between β -hydrogen transfer to afford a ketone [route (c)] and γ -hydrogen transfer to afford an alkene [route (d)] (Scheme 6). By analogy to ample previous findings on gaseous transition-metal alkoxides,^[14,25–28] a hydridometal species is proposed in route (d); note, however, that in the particular case of the $[(C_6H_4O_2)V(OR)(OR')]^+$ complexes studied here, a metal hydride does not need to be involved as an intermediate because hydrogen transfer can directly occur to the other alkoxy group.^[17] Within this framework for classification of the fragmentations observed experimentally, the reactions which lead to expulsions of neutral alcohols as well as carbonyl compounds are considered as belonging to route (c). Likewise, alkene losses are assigned to route (d). Similarly, the resulting consecutive products are attributed to the corresponding primary reactions of either routes, e.g. $\Delta m = -84$ in the case of $R^1, R^2 = OC_3H_7$ corresponds to the sequential elimination of two propene units. The last column of Table 2 shows the (normalized) ratio of the routes (c) and (d); other fragmentations, such as the loss of CH_3 from the dimethoxy derivative, are neglected in this

comparison. For almost all complexes studied here, the contribution of route (d) is much higher than that of route (c). Exceptions are $R^1, R^2 = CH_3$, of course, for which route (d) is impossible, and the ions containing an *isopropyl* unit for which the amount of route (c) is enhanced. When the competition among the substituents is considered, the β -hydrogen-transfer steps according to route (c) show a small discrimination between R^1 and R^2 with a slight preference for the elimination of the smaller alcohol. In contrast, route (d) is much more specific in that a high preference for the elimination of the larger alkene is observed. These differential substituent effects can be understood on the basis of the mechanisms proposed above. Thus, in route (c), one substituent must serve as hydrogen donor while the other one acts as hydrogen acceptor and is then lost as an alcohol. By such, the substituent effects counterbalance each other. In the olefin elimination according to route (d), however, only one alkoxy group is involved and formation of the more substituted alkene is favored, as expected.



Scheme 6.

Conclusion

Electrospray mass spectrometry allows the generation of cationic alkoxovanadium(v) complexes $[(C_6H_4O_2)V(OR^1)(OR^2)]^+$, bearing a catecholate unit ($C_6H_4O_2$) as ligand. For all vanadium(v) complexes described above, a trend for the preferential evaporation of hydrocarbon fragments from alkoxy groups larger than CH_3 is observed, followed by evaporation of neutral alcohol ligands (R^1OH and R^2OH). The subsequent fragments formed at elevated collision energies still contain the catecholato ligand, suggesting a common $[(C_6H_4O_2)VO]^+$ core. The results demonstrate that the bond between vanadium(v) and catechol is much stronger than those between the metal center and the alkoxy groups.

With respect to the role of vanadium in oxidation catalysis, the mass-spectrometric studies reported in this work suggest mononuclear vanadium(v) centers to be of limited use for the conversion of alcohols with β -H atoms into the corresponding carbonyl compounds because alkene elimination can obviously compete quite efficiently.

Experimental Section

The experiments were performed using a commercial VG BIO-Q mass spectrometer equipped with an ESI source followed by a tandem mass spectrometer of QHQ configuration (Q = quadrupole, H = hexapole).^[29] All examined ionized vanadium(v) complexes were generated by ESI of dilute methanolic solutions of $VOCl_3$, the appropriate alcohol(s), and catechol. All solutions were introduced

into the ESI source through a silica capillary with a syringe pump (3 μ L/min). For each ion studied, the instrument parameters were optimized for maximum ion abundances. Nitrogen was used as a nebulizer and drying gas at a source temperature of 80 °C. Collision induced dissociation (CID) experiments were performed with xenon as a collision gas at a pressure of approximately $3 \cdot 10^{-4}$ mbar, and several collision energies (E_{lab} from 0 to 30 eV). For the CID experiments, the ions were mass-selected using Q1, allowed to interact with the collision gas in the hexapole collision cell, and the ionic products were then analyzed by scanning Q2. The cations observed in all solvents used can be divided into two major categories: vanadium-containing cations and metal-free cations; the latter are of no interest in this study, except that they were tried to be kept minimal in order to increase the yields of metal-containing ions. For all species, the number of ligands of the formed solvated cations depends on the cone voltage in the ESI source which determines the softness or hardness of the ionization conditions. All vanadium(v) complexes presented here are formed at a cone voltage of $U_c = 20$ eV, which corresponds to gentle ionization conditions where multiply ligated ions prevail. At $U_c > 80$ V, diatomic VO^+ prevails for all mixtures studied.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 546), the Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin.

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Received February 21, 2005
Published Online: June 21, 2005