

Gas-Phase Fragmentation Behavior of Vanadium(V) Complexes Containing One Molecule of a C₄-Dicarboxylic Acid

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Complexes of vanadium(V) with C₄-dicarboxylic acids, i.e. maleic, fumaric, and succinic acid, are investigated by means of electrospray ionization (ESI) mass spectrometry. Under soft conditions of ionization, ESI of a diluted solution of OV-(OC₂H₅)₃ in methanol gives rise to complexes, which are best described by the general formula [(XCOO)₂VO(C₄H₄O)]⁺ (X = CH, CH₂), where the solvent employed delivers the (C₄H₄O) unit, whose components are either attached to vanadium as an intact methanol ligand or are distributed over the other atoms. In the complexes containing maleic or succinic acid, the acids appear to act as chelating ligands with coordination of the vanadium center by two oxygen atoms from two different carboxylic groups. In contrast, the *trans*-configuration in fumaric acid prevents the formation of similar chelate complexes. The fragmentation reactions of the

complexes are studied by collision-induced dissociation and labeling experiments. For the vanadium(V) complex derived from maleic acid, a preferential elimination of CO₂ is observed, followed by combined losses of CO₂, CO, and C₂H₂ or alternatively an intact C₄H₂O₃ unit, which most likely corresponds to maleic anhydride. Instead, evaporation of water followed by loss of carbon monoxide predominates for the corresponding V^V cation generated in the presence of succinic acid. Due to the fact that the loss of water involves the central methylene groups of succinic acid, a connection to the vanadium-oxide-mediated formation of maleic acid upon partial oxidation of C₄-hydrocarbons is proposed.

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Introduction

Transition metals and their oxides play important roles as catalysts exhibiting high selectivities and activities in many processes^[1] and therefore are widely used in chemical and petrochemical industries since more than a century. Among the transition-metal oxides, a particularly important class of catalysts are vanadium oxides, which are employed in several selective oxidations and also act as an important support material in numerous technical applications.^[2–7]

One of the most complex selective oxidation reactions is the conversion of *n*-butane to maleic anhydride on the surface of vanadyl-pyrophosphate oxide (VPO).^[8–10] In this reaction, eight hydrogen atoms are abstracted from the reactant and three oxygen atoms are added to eventually afford maleic anhydride as a product.^[11] Although the reaction has been extensively studied during recent years, the mechanistic knowledge is still limited, mainly because of the complexity of the oxidation as well as the fact that none of the potential reaction intermediates, such as butenes or

furane, have been observed among the reaction products under standard industrial conditions.^[12] Based on studies of reaction kinetics^[13,14] and on the observation of intermediates under non-standard conditions,^[13,15] the oxidation of *n*-butane to maleic anhydride has been proposed to proceed via two independent pathways.^[16] The first is referred to as the olefinic route, which involves a consecutive conversion of *n*-butane to butene and then to butadiene, followed by oxygenation of butadiene to form furane and the subsequent conversion of furane into maleic anhydride.^[9] For the olefinic route, the intermediate products were proposed to easily desorb from the oxidic surface of the catalyst. In contrast, on the basis of kinetic data Zhang-Lin et al.^[13,14] concluded that the main pathway for the formation of maleic anhydride from *n*-butane proceeds via metal-alkoxide species as key intermediates, which are able to maintain σ -bonds between the organic components and vanadium species present on the catalyst (“alkoxide route”). In this reaction sequence, the intermediate products do not leave the surface until completion of the reaction.^[17] Despite numerous studies aimed at gaining insight into the mechanisms, it is still not settled which route is preferred. Further, based on isotopic labeling studies, Chen and Munson^[18] presented direct evidence that the conversion of *n*-butane into maleic anhydride on VPO catalysts proceeds via two different mechanistic scenarios. Supported by NMR spectroscopic data, they suggested that both routes may occur simulta-

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neously to produce maleic acid, before conversion to the final product maleic anhydride is achieved. Using ^{13}C NMR, Chen and Munson recently proposed a single-site organometallic mechanism for the selective oxidation of *n*-butane on VPO catalysts.^[19] According to their conclusions, activated butane forms a chelating configuration on the surface of the catalyst by coordination of C(1) and C(4) of butane to vanadium species. The chelating configuration is kept during the reaction sequence until maleic anhydride is formed. The reaction model proposed by Chen and Munson can also account for a number of other previous observations, such as the formation of ethylene as a side product, for example. Control of the formation of side products during the production of maleic anhydride is a non-trivial problem. Various species are formed in different processes and both the presence and ratios of side products and intermediates depend on many factors, for example, the ratio of V/P in the VPO catalysts and the presence of gaseous oxygen.^[18] In particular, the formation of maleic anhydride is further associated with partial combustion leading to the formation of carbon oxides. In fact, the variety of intermediates and side products conceivable during the formation of maleic anhydride and their possible reactions with surface species render the complete understanding of the catalytic process rather difficult.

Information about mechanistic aspects in heterogeneous catalysis has been derived mainly from in-situ characterization of the catalysts and from observations of related processes which occur in solution or at liquid-solid or gas-solid interfaces. Recently, gas-phase studies of mass-selected cluster ions have been introduced as a complementary method for gaining information about the elementary steps of such reactions.^[20–22]

In this respect, vanadium(V) complexes are of interest because they may be formed as transients in alkane oxidation on vanadium oxides in general and in particular because they have been shown to be involved in the oxidation of *n*-butane to maleic anhydride.^[9,23] While most previous gas-phase studies on this topic have addressed the oxidation of hydrocarbons by gaseous vanadium-oxide ions,^[21,24–29] here, we approach the problem from the side of the putative products. Accordingly, we investigate the generation and the behavior of vanadium(V) complexes containing one molecule of either maleic acid, fumaric acid, or succinic acid, which contain the C_4 skeleton of *n*-butane. The investigation of the dissociation behavior of these complexes may in turn add to the understanding of the processes which occur during the production of maleic anhydride. The ions of interest were produced using electrospray ionization (ESI)

mass spectrometry,^[30] a technique which permits transfer of ionic complexes into the gas phase directly from solution, with a variable degree of desolvation or fragmentation. Accordingly, ESI has been used for the analysis of inorganic and organometallic systems,^[31–33] also including vanadium-oxide clusters.^[9,25,26,28,30]

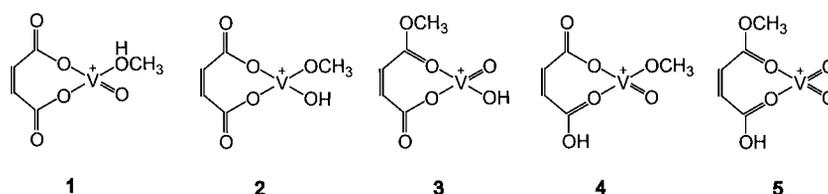
Results

Electrospray ionization of $\text{OV}(\text{OC}_2\text{H}_5)_3$ dissolved in methanol together with a small amount of maleic acid or succinic acid inter alia leads to the formation of vanadium(V) complexes which formally include a VO^+ unit originating from the metal precursor, one (doubly deprotonated) unit of the diacid, and one solvent molecule, i.e. formally corresponding to $[(\text{XCOO})_2\text{VO}(\text{C}_4\text{H}_4\text{O})]^+$ with $\text{X} = \text{CH}$ or CH_2 and the $(\text{C}_4\text{H}_4\text{O})$ unit stemming from the solvent. The precise connectivity of the complexes is unknown, however; specifically, it is not certain, how the $(\text{C}_4\text{H}_4\text{O})$ unit is distributed over the rest of the molecule. The first task is accordingly to investigate the types of ionic complexes formed. Given the components of the solutions used in ESI, structures 1–5 appear plausible for the case of maleic acid (Scheme 1); note that in addition to structures 1–5, various related arrangements are conceivable (e.g. interchange of coordination from the carbonyl to the ester oxygen atoms).

Before addressing the ion structures, we note that the abundances of the $[(\text{XCOO})_2\text{VO}(\text{C}_4\text{H}_4\text{O})]^+$ complexes strongly depend on the concentrations of $\text{OV}(\text{OC}_2\text{H}_5)_3$ as well as the acids. If the concentration of acid is too high, the positive ion mass spectra are dominated by proton-bound oligomers of the acid itself, such as $[(\text{CHCOOH})_2\text{H}]^+$ ($m/z = 233$) and $[(\text{CHCOOH})_3\text{H}]^+$ ($m/z = 349$) in the case of maleic acid ($\text{X} = \text{CH}$). Vice versa, the yields of the desired mononuclear carboxylato-vanadium(V) complexes are also poor when the concentration of triethoxovanadate(V) is too large, due to the formation of polynuclear metal complexes.

Complexes of Vanadium(V) with Maleic Acid

Under soft ionization conditions, ESI of a triethoxovanadate(V) solution in methanol with a trace of maleic acid provides an abundant signal at $m/z = 213$ which can be attributed to the above mentioned $[(\text{XCOO})_2\text{VO}(\text{C}_4\text{H}_4\text{O})]^+$ species. According to the structural proposals shown in Scheme 1, the vanadium(V) center is connected with maleic acid through oxygen atoms from both carboxy groups,



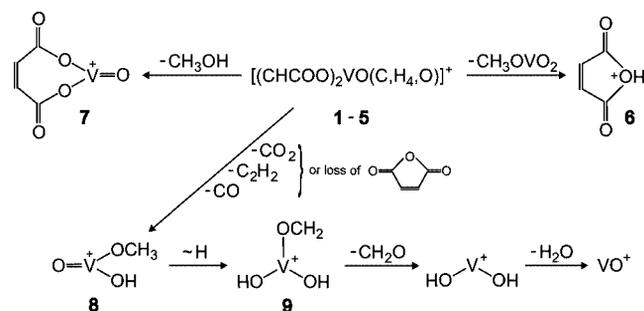
Scheme 1.

Table 1. Neutral losses (given as mass differences, Δm) observed upon CID of the mass-selected cations with $m/z = 213$ and 217 generated by ESI of $\text{OV}(\text{OC}_2\text{H}_5)_3$ and maleic acid in CH_3OH and CD_3OD , respectively. Data are given relative to the base peak (100) of the CID products at $E_{\text{lab}} = 5$ eV.

Δm	-18	-20	-30	-32	-36	-44	-58	-62	-74	-76	-98	-114	-117	-128	-130
m/z 213	20		5	13		100	11		19		50	2		6	
m/z 217		9		4	10	100		15		20	60		5		3

thereby forming a chelating configuration. The coordination shell is filled by an oxo- and a methanol ligand in the case of structure **1**, a hydroxy- and a methoxy group in structure **2**, an oxo- and a hydroxo group with the methyl group forming an ester with one carboxy unit, i.e. a complex of the singly deprotonated monomethyl ester of maleic acid with a $\text{V}(\text{O})(\text{OH})^+$ unit (structure **3**), the reverse arrangement of H and CH_3 in structure **4**, and finally H and CH_3 are both connected with oxygen atoms of the acid with two oxo ligands at vanadium, structure **5**. In all structures considered, the vanadium is coordinated by four oxygen atoms, and thus **1–5** only differ by the location of the hydroxyl group and the methyl group of the $(\text{C}_4\text{H}_4\text{O})$ unit.

The CID spectrum of the mass-selected ion with $m/z = 213$ produced upon ESI of a methanolic solution of triethoxovanadate(V) and maleic acid is dominated by the expulsion of neutral CO_2 ($\Delta m = -44$, Table 1). The next intense signal, corresponding to $\Delta m = -98$, can be assigned to a combined loss of CO_2 , CO , and C_2H_2 , suggesting a complete disintegration of the maleic acid attached as a ligand. Alternatively, this dissociation may involve the elimination of maleic anhydride as an intact $\text{C}_4\text{H}_2\text{O}_3$ entity. The latter conjecture is supported by the formation of protonated maleic anhydride (**6**) upon dissociation of the ion with $m/z = 213$ ($\Delta m = -114$, Scheme 2). As a result of the formal loss of neutral $\text{C}_4\text{H}_2\text{O}_3$, the cationic fragment ion $[\text{OV}(\text{OH})(\text{OCH}_3)]^+$ is proposed to be formed (structure **8** in Scheme 2). This ion undergoes subsequent isomerization via hydrogen migration from the methoxy ligand to the oxo group (**8** \rightarrow **9**) followed by elimination of CH_2O (thus, $\Delta m = -128$ in total) to yield the dihydroxo vanadium-cation $\text{V}(\text{OH})_2^+$, which can then expel water to finally afford the diatomic cation VO^+ .^[34] Minor dissociation pathways correspond to the expulsions of water ($\Delta m = -18$), formaldehyde ($\Delta m = -30$), methanol ($\Delta m = -32$), and the combined losses of methanol and acetylene ($\Delta m = -58$).



Scheme 2.

If deuterated methanol is used as a solvent, the mass of the precursor ion shifts to $m/z = 217$, and CID of this species shows a similar fragmentation pattern. The most notable shifts of the mass differences upon ion fragmentation are those expected for the reactions in which neutral methanol or its fragments, such as formaldehyde, are lost. In contrast, the mass difference $\Delta m = -98$ remains unchanged, consistent with the suggested formation of maleic anhydride without participation of the $(\text{C}_4\text{H}_4\text{O})$ unit.

With regard to the ion structures **1–5**, there are a few, indirect arguments in favor of the presence of isomers **2** and/or **4**. (i) For a methoxy ligand directly attached to a metal core, such as in structures **2** and **4**, there is ample evidence of prevailing redox reactions via β -hydrogen migrations which then provide neutral formaldehyde as a fragment ($\Delta m = -30$),^[35–37] even including cationic catecholovanadium(V) methoxides closely related to structure **2**.^[38] Further, the loss of methanol ($\Delta m = -32$) can easily occur from **2** and **4** after hydrogen migration to form isomer **1** followed by dissociation. (ii) While consideration of structures **2** and/or **4** provide an explanation for the minor losses of formaldehyde and methanol, respectively, the prevailing decarboxylation upon CID implies the presence of a carboxylato group from which CO_2 can be lost easily, which can occur for isomers **1–4** bearing carboxylato ligands.^[39–42] (iii) Structurally indicative are the competing losses of neutral CH_3OVO_2 and neutral $\text{C}_4\text{H}_2\text{O}_3$, which only differ by the location of the proton in the ionic product. Assuming the smallest amount of rearrangement prior to fragmentation, this is consistent with the presence of structures **1**, **2**, and **4**; in case of structure **4**, the loss of neutral methoxovanadium dioxide CH_3OVO_2 ($\Delta m = -114$) to afford protonated maleic anhydride can proceed from without any further hydrogen migrations prior to dissociation. (iv) Structures **3** and **5** derived from the monomethylester of maleic acid appear less likely, because the CID spectrum of the ion with $m/z = 213$ independently prepared from a solution of $\text{OV}(\text{OC}_2\text{H}_5)_3$ and the monomethyl ester in methanol is dominated by loss of methanol and, in particular, decarboxylation is only a very minor process. (v) Last but not least, structure **1** with a presumably loosely bound methanol unit appears less likely because predominating loss of CH_3OH would be expected upon CID, which is not the case in the experiment. As a general note of caution we add, however, that the assignment of the ion structure is further complicated by the fact that proton migrations may allow for a facile interconversion between the various isomers. Strictly speaking, no unambiguously distinction between isomers **1–5** can be made based on the CID experiments, and par-

ticularly the presence of a mixture of ion structures cannot be ruled out. Nevertheless, the CID data reported in Table 1 can be explained by the mechanism depicted in Scheme 2, which is also fully consistent with the labeling data. Further, the loss of methanol is suggested to afford the oxo complex **7**, whose CID spectrum has been recorded independently and is dominated by an expulsion of CO ($\Delta m = -28$) with minor pathways corresponding to losses of CO₂ ($\Delta m = -44$), two molecules of CO ($\Delta m = -56$), and maleic anhydride (or CO₂, CO, and C₂H₂, both $\Delta m = -98$) to afford bare VO₂⁺.

Notably, a mixture of OV(OC₂H₅)₃ and fumaric acid does not form a corresponding ion with $m/z = 213$ under ESI conditions, no matter which concentrations of the precursors were used. Specifically, the ESI solutions were prepared by mixing of 0.5 mL of methanolic triethoxovanadate solution (0.5 μ L triethoxovanadate in 10 mL methanol) with 0.5 mL of a solution of fumaric acid in methanol (different concentrations from 0.05 to 1 g of fumaric acid in 10 mL methanol were applied). As the same mixing ratios were used successfully in the cases of maleic and succinic acid, we conclude that the *trans*-configuration of fumaric acid prevents the formation of chelate rings with the cationic vanadium core.

Complexes of Vanadium(V) with Succinic Acid

Similar to the case of maleic acid, ESI of a dilute methanolic solution of succinic acid and triethoxovanadate(V) affords a monocationic complex with $m/z = 215$, which, by analogy, we attribute to one of the vanadium(V) species **10–14** shown in Scheme 3; again, a more definitive assignment cannot be made on the basis of the CID spectra.

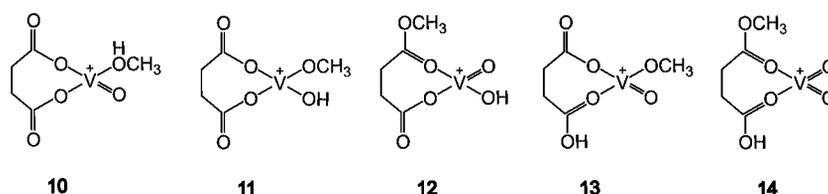
The CID spectrum of the mass-selected complex with $m/z = 215$ (Table 2) is dominated by eliminations of water ($\Delta m = -18$), methanol ($\Delta m = -32$), as well as a combined loss of CO and H₂O ($\Delta m = -46$). Minor dissociation pathways correspond to combined eliminations of CO₂ and H₂O ($\Delta m = -62$), CO₂, H₂O, and CO ($\Delta m = -90$), as well as CO₂, CO, and C₂H₄ ($\Delta m = -100$); again, the latter fragmentation can also be due to the loss of an intact unit, i.e. succinic anhydride in this case. As a result of these minor dissociation processes, the cation [OV(OH)(OCH₃)₃]⁺ is formed which already was observed in the case of the complex with maleic acid (structure **8** in Scheme 2) and which undergoes a subsequent loss of CH₂O (thus, $\Delta m = -130$ in total). Also similar to the complex derived from maleic acid, an expul-

sion of CH₃OVO₂ concomitant with formation of protonated succinic anhydride is observed as a minor channel ($\Delta m = -114$).

Table 2. Neutral losses (gives as mass differences, Δm) observed upon of CID of the mass-selected cations [A = (CH₂COO)₂VO-(C,H₄,O)]⁺, B = [(CD₂COO)₂VO(C,H₄,O)]⁺, and C = [(CH₂COO)₂-VO(C,D₄,O)]⁺ generated by ESI of OV(OC₂H₅)₃ and succinic acid in methanol using either unlabeled reagents or [2,2,3,3-D₄]-succinic acid and CD₃OD, respectively. Data are given relative to the base peak (100) of the CID products at $E_{\text{lab}} = 5$ eV.

Δm	A	B	C
-18	100		50
-19		46	38
-20		62	
-30	6		
-32	57	8	
-36			5
-46	43		100
-47		69	82
-48		100	
-62	12		21
-63		23	5
-64		31	
-90	14		25
-92		9	
-100	14		38
-101		33	
-103		31	
-104		15	
-114	7	4	
-117			17
-120	1		8
-122		8	
-130	7		
-132			5
-133		4	3
-134			2
-160	28		
-161		23	
-162		15	
-163			27
-164			17

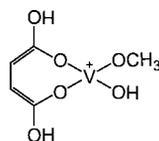
The experimentally observed mass difference $\Delta m = -46$ can be assigned to the expulsion of CO and H₂O, but it may also correspond to the loss of an ethanol molecule formed from the triethoxovanadate precursor. Hence, an additional labeling experiment was performed using (CD₂COOH)₂ as the acidic component. From methanolic solution of a mixture of triethoxovanadate(V) and (CD₂COOH)₂, the corresponding cation [(CD₂COO)₂VO-(C,H₄,O)]⁺, $m/z = 219$, is generated under soft ESI condi-



Scheme 3.

tions. The CID spectrum of mass-selected $m/z = 219$ shows a mass difference of $\Delta m = -48$ as the base peak (Table 2), which can thus be only assigned to a combined expulsion of CO and D₂O. The mass difference of $\Delta m = -47$ is accordingly attributed to a combined elimination of CO and HDO. The CID spectrum of [(CD₂COO)₂VO(C,H₄,O)]⁺ is further characterized by expulsions of HDO ($\Delta m = -19$), D₂O ($\Delta m = -20$), methanol ($\Delta m = -32$), respectively, as well as the combined losses of CO₂ and D₂O ($\Delta m = -64$), CO₂ and HDO ($\Delta m = -63$), CO₂, CO, and C₂HD₃ ($\Delta m = -103$), as well as CO₂, CO, and C₂D₄ ($\Delta m = -104$). Once more, the combined losses of carbon oxides and ethylene may also be assigned to the expulsion of an intact acid anhydride. In addition to the expulsions of H₂O ($\Delta m = -18$) and HDO ($\Delta m = -19$), the CID spectra of the mass-selected ion [(CH₂COO)₂VO(C,D₄,O)]⁺ generated from CD₃OD solution reveal preferential combined eliminations of CO and H₂O ($\Delta m = -46$) as well as CO and HDO ($\Delta m = -47$).

In comparison, the fragmentations of the complexes derived from maleic and succinic acid are closely related to each other. In both cases, the CID spectra are characterized by the eliminations of identical or very similar neutral fragments. In fact, the mechanism proposed in Scheme 2 can describe the dissociation reactions observed in both cases. The main difference is that for the complex derived from maleic acid the major fragmentations are associated with an expulsion of CO₂ ($\Delta m = -44$) and the elimination of C₄H₂O₃ ($\Delta m = -98$), whereas for the complex generated using succinic acid the most abundant fragmentations correspond to the elimination of water ($\Delta m = -18$) and the combined loss of H₂O and CO ($\Delta m = -46$). We note in passing that the pronounced loss of water from the complexes derived from succinic acid might be associated to contributions of enol forms as reaction intermediates, e.g. structure **15** (Scheme 4).

**15**

Scheme 4.

Complexes of Vanadium (V) with Acetic Acid

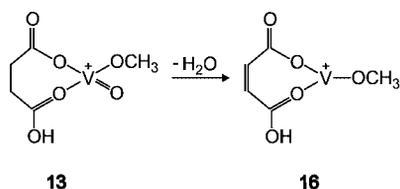
ESI of triethoxovanadate dissolved in methanol with up to 20% of acetic acid leads to the formation of various complexes containing vanadium as well as acetic acid. For comparison with the complexes derived from the diacids discussed above, we focus on the vanadium(V) complex containing a vanadyl cation, two (deprotonated) molecules of acetic acid, and one methanol unit, i.e. formally [(CH₃COO)₂V(O)(C,H₄,O)]⁺ ($m/z = 217$). Upon CID of the mass-selected complex with $m/z = 217$, the main process corresponds to the expulsion of neutral acetic acid ($\Delta m = -60$). Minor dissociation pathways are associated with the

expulsion of water ($\Delta m = -18$), methanol ($\Delta m = -32$), and a combined loss of water and acetic acid ($\Delta m = -78$). Like for all vanadium(V) complexes studied here, the formation of VO⁺ ($\Delta m = -150$) as a terminal fragment is observed at larger collision energies.^[43] In marked contrast to the complexes derived from maleic and succinic acid, however, no losses of carbon oxides are observed. Hence, consistent with the results obtained in the case of fumaric acid, the ability of maleic as well as succinic acid to form a chelating coordination to the vanadium center gives rise to a unique reactivity pattern. The fact that we can observe the complex with acetic acid, while the corresponding experiments with fumaric acid were not successful may be attributed to the experimental circumstances. Thus, due to the reasonable volatility of acetic acid, larger quantities of this compound can be added to the solution used in ESI and also gas-phase reactions occurring during the spray process may enhance formation of loosely bound ion/molecule complexes,^[44] e.g. the tautomeric structure [(CH₃COOH)(CH₃COO)V(O)-(OCH₃)]⁺ with an intact acetic acid ligand.

Mechanistic Implications

Most of the results reported here follow general expectations. Thus, among the major dissociation pathways for the V^V cations derived from maleic as well as succinic acid are routes leading to the formation of carbon oxides. Similar decarbonylations as well as decarboxylations of carboxylic acids are known ever since the beginning of organic chemistry, e.g. the Kolbe synthesis. Further, the apparent losses of the maleic and succinic anhydride as intact neutral fragments from the respective complexes is consistent with the way of ion generation, but does not provide further insight with regard to the production of maleic anhydride from butane.

Nevertheless, there is one specific aspect in the fragmentation patterns of the ion derived from succinic acid which deserves particular attention with respect to oxidation catalysis. Specifically, loss of water is found as the most abundant process upon low-energy CID of complex [(CH₂COO)₂VO(C,H₄,O)]⁺. Deuterium labeling in both ions, [(CD₂COO)₂VO(C,H₄,O)]⁺ and [(CH₂COO)₂VO(C,D₄,O)]⁺, demonstrates that the majority of the neutral water molecules lost incorporate H(D) atoms from the methylene groups of succinic acid, in that loss of D₂O ($\Delta m = -20$) prevails for [(CD₂COO)₂VO(C,H₄,O)]⁺, whereas expulsion of H₂O ($\Delta m = -18$) predominates in the case of [(CH₂COO)₂VO(C,D₄,O)]⁺ (Table 2). This finding implies that the central C–C bond undergoes dehydrogenation, thereby suggesting a possible connection from succinic to maleic acid in vanadium-mediated oxidations of hydrocarbons; an example for an illustration of this perspective is shown in Scheme 5 for the isomer **13** proposed to be involved for the ion formed upon ESI of the solution contained succinic acid, whose dehydration would lead from the V^V species **13** to the V^{III} complex **16**.



Scheme 5.

In a more general perspective of the butane oxidation to maleic anhydride, the obvious importance of chelating coordination by maleic as well as succinic acid supports the formation of surface-bound intermediates in the course of the oxidation reaction. Thus, the suggested alkoxide route or related pathways, which involve the formation of reaction intermediates covalently bound to vanadium surface species, find some analogy in the gas-phase chemistry of these systems.

Conclusions

Electrospray ionization mass spectrometry is applied for the generation of dicarboxylato-vanadium(V) complexes derived from maleic and succinic acid, respectively. The results suggest that acids which are capable of forming a chelate ligand bring about an efficient coordination with a vanadium(V) center under ESI conditions. Upon collision-induced dissociation of the V^V complexes, the expulsion of CO_2 is favored for the complexes derived from maleic acid, whereas a combined evaporation of H_2O and CO is preferred for the corresponding complexes formed from succinic acid. Interestingly, the dehydration observed in the latter case provides a connection between succinic and maleic acid, which has not been considered so far in mechanistic considerations regarding the partial oxidation of C_4 hydrocarbons to maleic anhydride on vanadia-based catalysts.

Experimental Section

The experiments were performed using a VG BIO-Q mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization source.^[45] The vanadium(V) complexes of interest were generated by ESI of dilute solutions of $OV(OC_2H_5)_3$ and the appropriate acids in methanol (or CD_3OD). The solutions were introduced into the ESI source via a silica capillary using a syringe pump at a flow rate of 5 $\mu L/min$ and a source temperature of 80 $^\circ C$ with nitrogen as nebulizing and drying gas. All data were collected and averaged over at least 20 scans. Collision-induced dissociation experiments were performed with Q1 mass-selected ions using xenon as a collision gas in the hexapole at a pressure of ca. 2×10^{-4} mbar and collision energies from $E_{lab} = 0-30$ eV, while analyzing the ionic products by scanning Q2.

Although many different cations of rather broad stoichiometric compositions are formed from the solutions studied by ESI, we were interested only in complexes containing a single vanadium(V) and one molecule of the corresponding diacid. The number of ligands of the solvated cations is crucially dependent on the cone voltage of the ESI source.^[45-48] All vanadium(V) complexes presented here are formed under comparably soft conditions of ioniza-

tion, i.e. at cone voltages between 20 and 40 V, where multiply ligated ions predominate; at cone voltages above 80 V, diatomic VO^+ prevails for all mixtures studied.^[43]

Acknowledgments

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