

Intrinsic Mechanisms of Oxidation Reactions as Revealed by Gas-Phase Experiments

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Abstract Oxidation catalysis is of extreme importance in many areas of chemistry. The intrinsic mechanisms of oxidation reactions are, however, quite often understood only rather poorly, and catalyst research is mostly, if not exclusively, based on entirely empirical approaches. In this respect, gas-phase experiments can provide a complementary approach in that they can allow the investigation of the elementary processes in oxidation catalysis step by step. By such, some general insight can be obtained, which may assist in the development of more efficient oxidation catalysts.

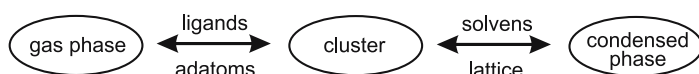
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1 Introduction

Selective partial oxidation of hydrocarbons poses considerable challenges to contemporary research. While by no means all, most catalytic oxidations are based on transition-metal oxides as active intermediates, and the oxidative dehydrogenation of ethylbenzene to styrene over potassium-promoted iron oxides at a scale of about 20 Mt/year may serve as an example [1]. Despite this

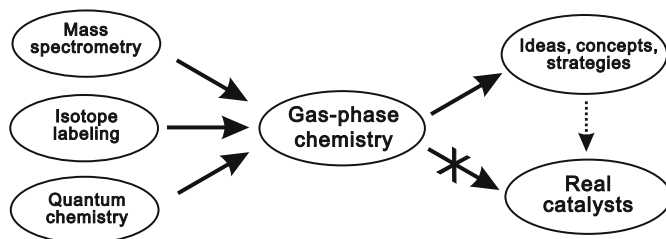
huge interest, detailed knowledge about the molecular mechanisms in oxidation catalysis is still limited, and catalyst improvement is often merely based on trial and error procedures.

Experimental and theoretical studies of ion/molecule reactions of transition-metal oxide ions have uncovered several reactions that permit the oxygenation of methane to methanol on a molecular scale [2]. If it were possible to upscale such a catalytic oxidation of methane from the laboratory to an industrial process, the enormous resources of CH₄ available either as natural gas or from biologic sources could be used more efficiently [3, 4]. In addition to oxygenation, the oxidative coupling of methane to larger hydrocarbons is also of considerable interest. Accordingly, fundamental studies on the mechanistic details in oxidation catalysis and the nature of the elementary steps involved can aid and perhaps even direct catalyst development. One approach to gain more profound insight into the fundamental steps in oxidation catalysis is to study well-designed and properly defined ion/molecule reactions in the idealized gas phase. Among others, one obvious advantage of this approach is the possibility of a direct comparison of experimental data with results obtained using adequate theoretical methods. A first link between small, often only diatomic, model systems to applied catalysis can be provided by the investigation of metal-oxide clusters. Further, inclusion of ligand effects and of the influences of solvent molecules can mimic processes occurring in homogenous catalysis. Likewise, inclusion of adatoms and possible lattice effects may link gas-phase studies and surface science in applied catalysis (Scheme 1).



Scheme 1

Despite the promise of gas-phase studies, at the very outset it needs to be clarified that the results obtained in gas-phase experiments (e.g., thermodynamic data, rate constants, selectivities, or isotope effects) cannot be expected



Scheme 2

to be directly transferable to applied catalysis. Instead, the emphasis is on describing the trends, concepts, or strategies (Scheme 2). Factors affecting regioselectivities, understanding the tuning of ligand effects, the role of counter ions, or the order of reduction and re-oxidation steps are all more likely to be comparable in the gas phase and in applied catalysis.

2

General Mechanistic Considerations in Oxidation

2.1

Thermochemical Boundaries

Any catalytic sequence needs to fulfill certain thermochemical boundary conditions as far as the elementary steps are concerned. For illustration, consider the oxygenation of an organic substrate *S* by a transition-metal oxo species [M]O according to reaction 1, where [M] stands for a bare or ligated, neutral or charged metal fragment:



In order to render the occurrence of reaction 1 exothermic, the bond strength of the oxidant, $D([\text{M}] - \text{O})$ needs to be lower than $D(\text{S} - \text{O})$ of the substrate. For most organic reactants, the energies gained upon oxygenation range from 350 to 450 kJ/mol [5–8]. Hydroxylation of methane, for example, liberates 375 kJ/mol ($\text{CH}_4 \rightarrow \text{CH}_3\text{OH}$), and even 428 kJ/mol are released upon hydroxylation of benzene ($\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{OH}$). Similarly, epoxidation of ethene liberates 354 kJ/mol ($\text{C}_2\text{H}_4 \rightarrow c\text{-C}_2\text{H}_4\text{O}$), and 472 kJ/mol are released when the O-atom transfer to ethene leads to the more stable acetaldehyde isomer ($\text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CHO}$). As a consequence, $D([\text{M}] - \text{O})$ should not exceed 450 kJ/mol, and even more efficient oxidation sequences are expected for more weakly bounded metal-oxo species.

On the other hand, the re-oxidation step required to convert the reduced form of the catalyst into the active species also sets some thermochemical boundaries, because only stoichiometric oxidation can be expected, if $D([\text{M}] - \text{O})$ is too low. With regard to the most conceivable terminal oxidants, O_2 , N_2O , or H_2O_2 , a bond strength in the order of $D([\text{M}] - \text{O}) \approx 250$ kJ/mol appears as a minimum for successful re-oxidation [7]. Hence, promising candidates for oxidation catalysis should have bond strengths that meet both boundaries, i.e., $D([\text{M}] - \text{O})$ should lie between 250 and 450 kJ/mol, where values closer to the lower limit are required in the particularly challenging case of alkane hydroxylation. Reviewing the existing data for metal-oxo bond strengths of gaseous transition-metal compounds, the most promising candidates appear to be either monoxides of late 3d transition metals or high-valent metal di-, tri-, or even tetroxides [7].

It should be clearly pointed out, however, that these considerations so far only concern mere thermodynamic effects without addressing any kinetic aspects. A particularly instructive example in this respect is the usage of N_2O as a terminal oxidant in the gas phase. From a mere thermochemical point of view, N_2O has a rather low O-atom affinity and can hence transfer its oxygen atom to all metal species with $D([\text{M}] - \text{O}) > 167 \text{ kJ/mol}$. Experimentally, it turns out, however, that many atomic metal ions experience a considerable kinetic hindrance with regard to O-atom transfer from N_2O [9, 10]. Despite the considerable bond strength of $D(\text{Cr}^+ - \text{O})$ at 360 kJ/mol [6], bare Cr^+ , for example, does not undergo any reaction with N_2O at thermal conditions. Hence, experimental studies explicitly addressing the re-oxidation step also form a key aspect in the development of a more comprehensive understanding of oxidation catalysis [11].

2.2

Two-State Reactivity

Despite its seeming simplicity and its obviously limited relevance for applied catalysis, the reaction of diatomic FeO^+ with dihydrogen has received quite some attention [12–21]. This particular interest is due to several experimental observations that give a somewhat confusing picture upon first sight [18]. Thus, the reaction of FeO^+ with H_2 proceeds only once in about 100 collisions, but yet shows the typical negative temperature dependence of exothermic gas-phase ion/molecule reactions. While such a behavior may be rationalized by involving the oxidation of dihydrogen as rate-determining step, the reaction does not show a particularly pronounced kinetic isotope effect. This in turn suggests that H–H bond cleavage is not involved in the rate-determining step. Accordingly, the FeO^+/H_2 system has been extensively studied by both experiment and theory. A mechanistic solution for the seemingly contradicting experimental findings was provided by ab initio calculations [14, 16, 17, 19–21]. These computational studies demonstrated that even though the overall reaction is spin allowed – both Fe^+ and FeO^+ have sextet ground states, and H_2 as well as H_2O are singlets – the crucial insertion intermediate HFeOH^+ has a quartet ground state and, even more importantly, the lowest-lying transition structure corresponds to a quartet (Fig. 1).

These state orderings lead to a situation in which the reactants and products belong to one spin surface, while the intermediates have a different spin multiplicity. The experimental and theoretical evidence indicates that for iron, as a 3d element, the spin-change itself is mediated by spin-orbit coupling and is in fact rate-determining for the occurrence of the overall reaction; this scenario can account for all experimental observations.

The detailed studies of this particular, rather simple reaction also formed the basis for the generalized concept of two-state reactivity [22], according to which thermal reactions are not necessarily confined to the spin

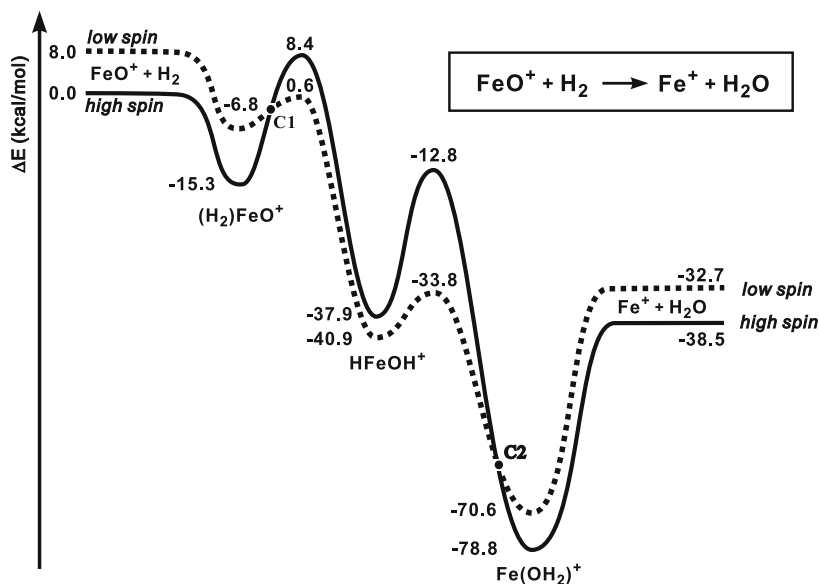


Fig. 1 Simplified potential-energy surface of the FeO^+/H_2 system

surface of the electronic ground-state, but rather spin-crossing effects can dramatically affect many features of numerous organometallic transformations. Thus, a number of other gas-phase oxidations mediated by the FeO^+ cation also involve changes of spin multiplicity as a key step [23, 24]. Further, two-state scenarios play a crucial role in the gas-phase reactions of other metal-oxide ions. In the case of the gas-phase oxidation of simple alkanes by the VO_2^+ cation, for example, small structural variations of the hydrocarbon substrates lead to drastic changes in product distributions, which can be attributed to the decisive role of spin changes for product formation with these substrates [25, 26].

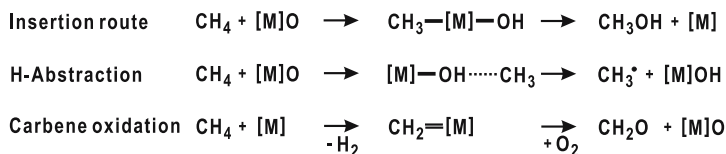
In subsequent research, it turned out that two-state reactivity can also provide a concept for the understanding of oxidation reactions way beyond the scope of gas-phase ion chemistry and can actually resolve a number of existing mechanistic puzzles. In enzymatic oxidations involving cytochrome P450, for example, changes in spin multiplicity appear to act as a kind of mechanistic distributor for product formation [27–29], and in the case of manganese-catalyzed epoxidation reactions, two-state scenarios have been put forward to account for the experimentally observed stereoselectivities [30–32]. Two-state reactivity is not restricted to oxidation reactions, and similar scenarios have been proposed for a number of other experimentally studied reactions of 3d metal compounds [33–37]. Moreover, two-state scenarios have recently also been involved in the chemistry of main group elements [38]. The concept of two-state reactivity developed from the four-atomic system FeO^+/H_2

in the idealized gas phase has hence turned out as a rather useful, wide-ranging paradigm in chemistry [39–43]. As far as O-atom transfer reactions by $[M]O^+$ cations are concerned, the gas-phase studies allow some rather general conclusions. Thus, most monoxides of middle and late transition metals bear high-spin ground states and the passage via low-energy pathways for bond activation requires the occurrence of a spin flip and thus involves two-state reactivity. While spin inversion is facile for 4d and particularly 5d elements, the change of spin multiplicity may be rate-determining in the case of 3d metals.

3 Mononuclear Metal-Oxide Ions

3.1 Oxidation of Methane

Gas-phase studies revealed the existence of two distinctly different mechanistic routes for the oxygenation of methane to methanol by a metal-oxo species (Scheme 3). The first variant proceeds via an addition of a C–H bond of methane across the $[M]O$ unit to yield an insertion species of the type $CH_3-[M]-OH$ as a reaction intermediate, from which methanol can be liberated via reductive elimination. Alternatively, the metal oxide can act as a mere hydrogen atom abstractor without any interaction between the metal and carbon centers, which requires that the newly formed O–H is stronger than the C–H bond of methane. Experimentally, these two routes can be distinguished by means of the associated kinetic isotope effects (KIEs) for C–H versus C–D bond activation. Thus, the FeO^+ cation, which reacts via the insertion route, bears a KIE of about 4.6 in the reaction with CH_2D_2 [44]. For the high-valent iron oxide cation $OFeOH^+$ an even larger KIE is found [45]. Somewhat lower, but still rather significant KIEs have been observed for MgO^+ ($KIE = 2.1$) [46] as well as MoO_3^+ ($KIE = 2.0$) [47]. In contrast, the $V_4O_{10}^+/CH_2D_2$ system, which can be regarded as a prototype of a simple hydrogen-atom abstraction mechanism, shows a KIE of only 1.35 [48], which is similar to the KIE of about 1.3 for the H(D)-atom abstraction from methane by free OH radicals [49].



Scheme 3

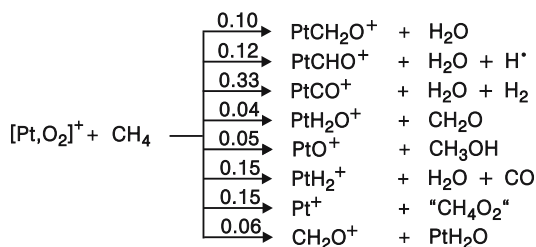
Another conceptual route for the oxygenation of methane begins with the exclusive activation of methane by a transition-metal ion followed by oxidation of the primary product with a suitable oxygen donor. Due to relativistic effects operating in the formation of metal-carbon multiple bonds [50], several bare cations of 5d elements, for example, are able to dehydrogenate methane under formation of the corresponding metal-carbene cations MCH_2^+ ($M = Ta, W, Os, Ir, Pt$) [2]. These MCH_2^+ species can subsequently undergo oxygenation reactions. Thus, the $PtCH_2^+$ cation reacts with molecular oxygen to afford oxygenation products such as the couple $PtO^+ + CH_2O$, of which the former is able to convert methane into methanol [51, 52]. Also noteworthy in this context is the (stoichiometric) coupling of methane and carbon dioxide to ketene, in which $TaCH_2^+$ is formed as the key intermediate from bare Ta^+ and methane [53, 54].

3.2

The Selectivity Problem

The particularly high reactivity of gaseous metal-oxide cations is, of course, also associated with some drawbacks. Thus, several metal-oxo species predicted to be rather reactive are on the other hand quite difficult to generate in yields and purities sufficient for ion-reactivity studies. Thermochemical as well as theoretical data suggest, for example, that the diatomic copper-oxide cation CuO^+ should be highly reactive with regard to both H atom abstraction as well as oxygen atom transfer [55]. Nevertheless, diatomic CuO^+ by so far has not yet been made in yields that permit further reactivity studies. Moreover, there has evolved a general problem in chemical reactivity, because highly reactive species that are capable of activating rather robust substrates, such as methane, often bear disappointing selectivities when it comes to even slightly more complex substrates. Thus, bare FeO^+ is capable of activating methane, but already with propane as a substrate, the discrimination between primary and secondary C-H bonds is rather poor [56, 57], and with transition-metal dioxide cations the site-selectivities often even decrease further [58, 59]. The reaction of the PtO_2^+ cation with methane may serve as a particularly impressive example in that this pair of reactants affords no less than eight different product channels with a substrate as simple as methane (Scheme 4) [59].

Another related problem is associated with over-oxidation of the substrate, in the extreme case resulting in complete combustion. In the case of methane oxidation by FeO^+ , for example, the activation of methane occurs with about 10% of the gas-kinetic collision rate, whereas those of the putative oxygenation products CH_3OH , CH_2O , and $HCOOH$ occur on every collision [60]. With regard to applied catalysis this would imply that the oxidation products are oxidized faster by about one order of magnitude compared to methane as the initial substrate. In the particular context of heterogeneous oxidation

**Scheme 4**

catalysis it is also to be expected that the polar, oxygenated products bear much larger residence times on the catalyst than the non-polar methane, thereby even further increasing the propensity of over-oxidation.

One way to address the selectivity problems outlined above is the deliberate usage of ligand effects. In the case of the copper-oxide cation, for example, the introduction of an additional phenanthroline (phen) ligand permits the generation of the ligated (phen)CuO⁺ cation in yields sufficient for reactivity studies, and this ligated cation is in fact able to activate small hydrocarbons such as propane [61]. We note in passing that for (phen)CuO⁺ also, the hydroxylation of propane involves a two-state scenario. Likewise, additional ligands have been used successfully for the modification of the reactivity of other metal-oxide cations [62–64]. Inversion of the sequence of oxidation and interaction with the substrate can also increase oxygenation yields [65]. In many cases, however, either the oxidation activity of the metal-oxo species is quenched by the ligand or the ligand itself undergoes oxidation upon attachment to the metal core. Nevertheless, reactivity studies of ligated metal-oxo species in the gas phase form a promising area for future research.

4

Gas-Phase Catalysis

Experiments conducted with mass-selected ions do not bear any direct relevance for applied catalysis, simply because the number densities of the ionic species are rather low (typically about 10⁶ particles per cm³). Nevertheless, the advantages associated with the handling and the detection of ionic species render gas-phase studies as an ideal tool for the investigation of the elementary steps in oxidation reactions. In the same vein, this holds true for the investigation of the separate mechanistic steps, and in appropriate mass spectrometers that are able to store ions for extended timescales this can also be extended to real catalytic cycles [66]. The time-honored prototype of such a catalysis was reported by Kappes and Staley who demonstrated that bare Fe⁺ ions initiate a catalytic conversion of CO into CO₂ in the presence of N₂O [67]. In the following decades, a number of other catalytic cycles involv-

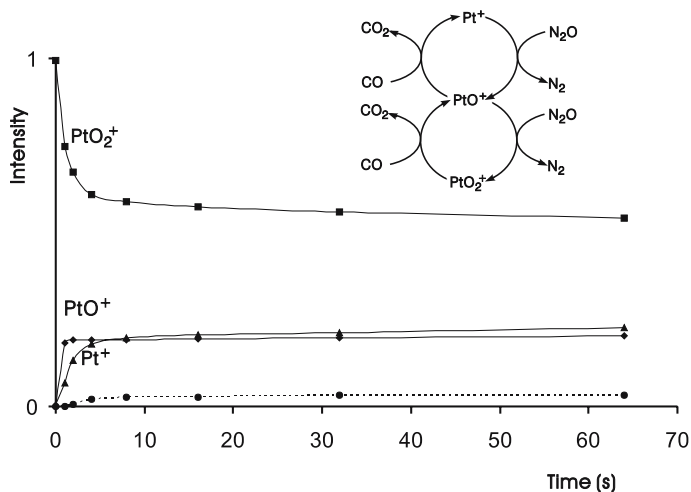


Fig. 2 Time-dependent intensity profiles of Pt^+ (\blacktriangle), PtO^+ (\blacklozenge), PtO_2^+ (\blacksquare), and the sum of all side products (\bullet) when reacting mass-selected $[\text{Pt}, \text{O}_2]^+$ with a mixture of N_2O and CO . The *inset* shows the two different catalytic cycles involved

ing gaseous FeO^+ were reported [44, 63, 68, 69]. Figure 2 shows an example of such a gas-phase catalysis, in which gaseous Pt^+ initiates two catalytic cycles for the oxidation of CO to CO_2 with N_2O as an oxidant. In this example, the turnover number is only limited by reactions with impurities present in the supplied gases or in the background vacuum of the mass spectrometer.

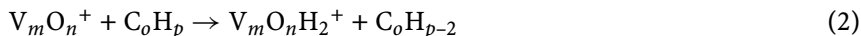
Beyer and coworkers later extended these reactions to platinum clusters Pt_n^+ and have demonstrated that similar reaction sequences for the oxidation of carbon monoxide can occur with larger clusters [70]. In addition, they were able to demonstrate poisoning effects as a function of surface coverage and cluster size. A related sequence for Pt_n^- anions was proposed by Shi and Ervin who employed molecular oxygen rather than N_2O as the oxidant [71]. Further, the group of Bohme has screened the mononuclear cations of almost the entire transition metal block for this particular kind of oxidation catalysis [72, 73]. Another catalytic system has been proposed by Waters et al. in which a dimolybdate anion cluster brings about the oxidation of methanol to formaldehyde; with nitromethane, however, a rather unusual terminal oxidant was employed [74].

5 Metal-Oxide Clusters

It goes without saying that mononuclear metal-oxo species can only be considered as first-order models for the processes occurring in partial oxidations

on heterogeneous catalysts. In fact, it has been questioned whether the reactions of a diatomic species, such as FeO^+ , can at all mimic the reactions occurring in real oxidation catalysis. Compared to the reactions of mononuclear species, the knowledge about the gas-phase reactivities of transition-metal oxide cluster ions is still quite limited. Nevertheless, considerable achievements have been obtained in recent years, mostly dealing with vanadium, nickel, platinum, silver, and gold.

Castleman and coworkers have initiated systematic studies of V_mO_n^+ ions with a broad variety of neutral substrates [75], not only including hydrocarbons [76–78], as well as methanol [79], but also other reagents such as haloalkanes [80–82]. Moreover, these experimental studies were recently augmented by inclusion of *ab initio* investigations of the key intermediates, thereby providing a rather profound insight into the gas-phase chemistry of transition-metal oxide clusters [83]. It is to be noted, however, that the instrumental setup used in the earlier studies of Castleman and coworkers had a somewhat limited mass resolution and some results needed to be revised later [78]. Nevertheless, these studies have provided a wealth of knowledge so far unachieved in the gas-phase chemistry of transition-metal oxide-clusters.



A reaction of particular relevance with respect to applied catalysis is the oxidative dehydrogenation (ODH) of hydrocarbon by V_mO_n^+ ions according to reaction 2, which involves a two-electron reduction of the cluster. By means of a systematic study of the reactions of various V_mO_n^+ ions as well as the related oxo-vanadium hydroxides $\text{V}_m\text{O}_n\text{H}^+$ ions with a set of C_4 -hydrocarbons, it was demonstrated recently that the ODH activity of the cluster ions shows a clear correlation with the formal valence of vanadium in the cluster ions with a maximum reactivity for formal vanadium (V) (Fig. 3) [84]. In such a kind of reactivity screening, it is essential to include more than a single reagent as a probe for the reactivity of the different ions in order to reduce interferences by kinetic barriers of one particular combination of neutral and ionic reactants [85]. Accordingly, the sums of the relative rate constants for the ODH reactions of the four different butenes are considered and normalized to the most reactive ion studied, which turns out to be the formally pure vanadium (V) compound V_3O_7^+ . In addition to isomeric butenes, *n*-butane was also studied, but has not been included in the screening, because of all ions investigated only $\text{V}_4\text{O}_{10}^+$ reacts with the saturated alkane.

These results further prompted *ab initio* investigations of the reactions of V_3O_7^+ and $\text{V}_4\text{O}_{10}^+$ with hydrocarbons. Thus, in a model study of the reactions of V_3O_7^+ with propane and 1-butene it was found that the initial C–H bond activation of the substrate acts as the rate-determining step. In the case of the saturated hydrocarbon C_3H_8 , the associated barrier is slightly

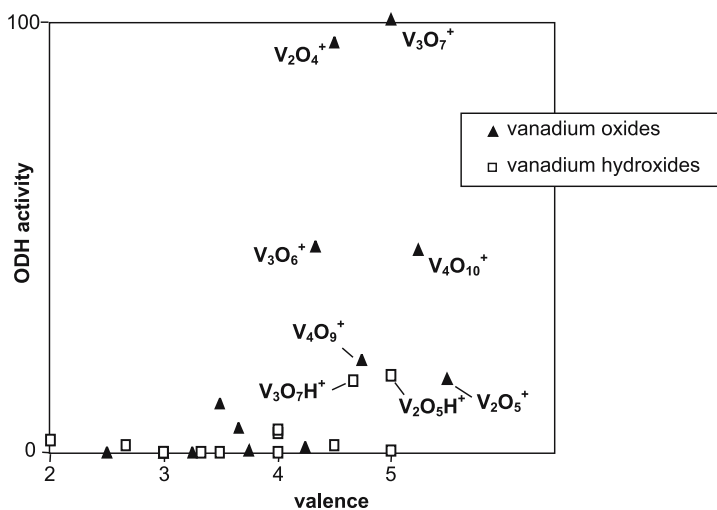
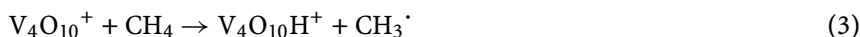


Fig. 3 ODH activities for 1-butene, *cis*-butene, *trans*-butene, and *iso*-butene versus the formal valence of vanadium in the $V_mO_nH_o^+$ clusters

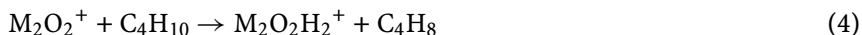
too high for the occurrence of bond activation at room temperature. However, the weaker allylic C – H bond in 1-butene, in conjunction with the larger energy gain upon complexation of the unsaturated hydrocarbon by the metal-oxide cations, promotes a rapid oxidation of the neutral substrate according to reaction 2 [86]. In marked contrast, the formally hypervalent cation radical $V_4O_{10}^+$ is even capable of activating methane under thermal conditions (reaction 3) [48]:



A detailed theoretical analysis further revealed that this reaction can be considered to proceed as a barrier-free H atom abstraction without any significant additional interaction between the methyl radical formed and the remaining cluster ion. Consistent with this mechanistic interpretation, the kinetic isotope effect associated with C – H(D) bond activation of CH_2D_2 is rather low ($KIE = 1.35$).

The oxidation of CO to CO_2 by metal-oxide clusters has received quite some attention, in part due to its relevance for the catalytic converters in automobiles, in part also because carbon monoxide is often used as a probe molecule in surface science and the reasonable simplicity of the system may still permit adequate theoretical treatments. In addition to the various systems involving $Pt_mO_n^+$ cations as well as $Pt_mO_n^-$ anions (see above), considerable efforts have been devoted to cluster anions of silver and gold, as reviewed recently [87]. A particular highlight is a conceptual catalytic cycle for the Au_2^- -mediated oxidation of CO with molecular oxygen, for which

the reaction intermediates were carefully characterized by experiment and theory [88]. Also in the context of exhaust-gas treatment, Castleman and coworkers have investigated the behavior of Ni_mO_n^+ cations towards nitric oxides [89]. As far as oxidations of organic substrates are concerned, more recent results have been obtained for the dinuclear clusters Mg_2O_2^+ [46], Fe_2O_2^+ [90], and Ni_2O_2^+ [91] and a series of M_2O_n^- anions ($n = 3, 4$) [92]. In general, the metal-oxide cluster ions turn out to be considerably less reactive than their mononuclear congeners. Thus, MgO^+ , FeO^+ and NiO^+ are all capable of activating methane, whereas none of the corresponding dinuclear M_2O_2^+ clusters can fulfill this task. Nevertheless, these clusters are still able to dehydrogenate other small hydrocarbons such as butane (reaction 4 with $M = \text{Mg, Fe, and Ni}$):



Quite obviously, however, further work – both experimental and computational – is needed to understand the behavior of metal-oxide clusters in more detail and thereby to identify reactive clusters, with options to also tune their reactivity by changing the cluster size. In this context, a final aspect should be mentioned briefly, which is related to the generation of metal-oxide cluster ions in the gas phase. The most common approach involves the use of a Smalley-type source in which a laser beam evaporates a metal followed by subsequent aggregation in an (oxidant-doped) supersonic expansion of a suitable gas (usually helium). It has been demonstrated, however, that these conditions can lead to the formation of dioxygen complexes rather than the desired high-valent metal-oxide clusters [93–95]. Direct laser desorption of solid metal oxides can be used as an alternative approach [92], but ion yields are only moderate and the instrumentation is considerably contaminated by the ablated material. However, this technique is unique in some respects and the prospects for the gas-phase chemistry of actinides [96] are particularly noteworthy. Other approaches involve the oxidation of pure metal cluster ions in the gas phase [97], but this approach is often associated with degradation of the clusters to smaller, if not even mononuclear entities [98, 99]. We have recently introduced a completely different approach based on electrospray ionization of appropriate inorganic precursors and so far have produced several M_mO_n^+ clusters for the metals magnesium, vanadium, and iron [46, 84, 100, 101]. The successful generation of binary metal-oxide clusters requires, however, that the bonds to the outer inorganic and organic ligands are weaker than those of the metal-oxide core, and thus related strategies have failed in the generation of Ti_mO_n^+ and Zn_mO_n^+ from seemingly suitable molecular precursors [102, 103].

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References

1. Weiss W, Schlögl R (2000) *Top Catal* 13:75
2. Schwarz H, Schröder D (2000) *Pure Appl Chem* 72:2319
3. Lunsford JH (2000) *Catal Today* 63:165
4. Labinger JA (2004) *J Mol Catal* 220:27
5. Berkowitz J, Ellison GB, Gutman D (1994) *J Phys Chem* 98:2744
6. Freiser BS (ed) (1996) *Organometallic ion chemistry*. Kluwer, Dordrecht
7. Schröder D, Shaik S, Schwarz H (2000) *Struct Bond* 97:91
8. Linstrom PJ, Mallard WG (eds) (2005) NIST chemistry webbook NIST standard reference database number 69, version June 2005
9. Kappes MM, Staley RH (1981) *J Phys Chem* 85:942
10. Lavrov VV, Blagojevic V, Koyanagi GK, Orlova G, Bohme DK (2004) *J Phys Chem A* 108:5610
11. Blagojevic V, Koyanagi GK, Caraiman D, Blagojevic V, Bohme DK (2002) *J Phys Chem A* 106:4581
12. Schröder D, Fiedler A, Ryan MF, Schwarz H (1994) *J Phys Chem* 98:68
13. Clemmer DE, Chen Y-M, Khan FA, Armentrout PB (1994) *J Phys Chem* 98:6522
14. Fiedler A, Schröder D, Shaik S, Schwarz H (1994) *J Am Chem Soc* 116:10734
15. Baranov V, Javahery G, Hopkinson AC, Bohme DK (1995) *J Am Chem Soc* 117:12801
16. Shaik S, Danovich D, Fiedler A, Schröder D, Schwarz H (1995) *Helv Chim Acta* 78:1393
17. Danovich D, Shaik S (1997) *J Am Chem Soc* 119:1773
18. Schröder D, Schwarz H, Clemmer DE, Chen Y-M, Armentrout PB, Baranov VI, Böhme DK (1997) *Int J Mass Spectrom Ion Processes* 161:177
19. Filatov M, Shaik S (1998) *J Phys Chem A* 102:3835
20. Irigoras A, Fowler JE, Ugalde JM (1999) *J Am Chem Soc* 121:8549
21. Matxain JM, Mercero JM, Irigoras A, Ugalde JM (2004) *Mol Phys* 102:2635
22. Schröder D, Shaik S, Schwarz H (2000) *Acc Chem Res* 33:139
23. Harris N, Shaik S, Schröder D, Schwarz H (1999) *Helv Chim Acta* 82:1784
24. Shiota Y, Yoshizawa K (2003) *J Chem Phys* 118:5872
25. Harvey JN, Diefenbach M, Schröder D, Schwarz H (1999) *Int J Mass Spectrom* 182/183:85
26. Engeser M, Schlangen M, Schröder D, Schwarz H, Yumura T, Yoshizawa K (2003) *Organometallics* 22:3933
27. Shaik S, Filatov M, Schröder D, Schwarz H (1998) *Chem Eur J* 4:193
28. Shaik S, de Visser SP, Ogliaro F, Schwarz H, Schröder D (2002) *Curr Opin Chem Biol* 6:556
29. Schoeneboom JC, Cohen S, Lin H, Shaik S, Thiel W (2004) *J Am Chem Soc* 126:4017
30. Adam W, Roschmann K, Saha-Möller CR (2000) *Eur J Org Chem* 3519
31. Brandt P, Norrby PO, Daly AM, Gilheany DG (2002) *Chem Eur J* 8:4299, and references cited therein
32. Cavallo L, Jacobsen H (2003) *J Phys Chem A* 107:5466
33. Fiedler A, Schröder D, Zummack W, Schwarz H (1997) *Inorg Chim Acta* 259:227
34. Kretzschmar I, Schröder D, Schwarz H, Rue C, Armentrout PB (1998) *J Phys Chem A* 102:10060
35. Rue C, Armentrout PB, Kretzschmar I, Schröder D, Harvey JN, Schwarz H (1999) *J Chem Phys* 110:7858
36. Bärsch S, Kretzschmar I, Schröder D, Schwarz H, Armentrout PB (1999) *J Phys Chem A* 103:5925

37. Hess JS, Leelasubcharoen S, Rheingold AL, Doren DJ, Theopold KH (2002) *J Am Chem Soc* 124:2454
38. Perez P, Andres J, Safont VS, Contreras R, Tapia O (2005) *J Phys Chem A* 109:4178
39. Plattner DA (1999) *Angew Chem Int Ed* 38:82
40. Harvey JN, Poli R, Smith KM (2003) *Coord Chem Rev* 238/239:347
41. Poli R, Harvey JN (2003) *Chem Soc Rev* 32:1
42. Schwarz H (2004) *Int J Mass Spectrom* 237:75
43. Shaik S, Cohen S, de Visser SP, Sharma PK, Kumar D, Kozuch S, Ogliaro F, Danovich D (2004) *Eur J Inorg Chem* 207
44. Schröder D, Schwarz H (1990) *Angew Chem Int Ed Engl* 29:1433
45. Schröder D, Schwarz H (1991) *Angew Chem Int Ed Engl* 30:991
46. Schröder D, Roithová J (2006) *Angew Chem Int Ed* (in press), published online 21 July 2006
47. Kretzschmar I, Fiedler A, Harvey JN, Schröder D, Schwarz H (1997) *J Phys Chem A* 101:6252
48. Feyel S, Döbler J, Schröder D, Sauer J, Schwarz H (2006) *Angew Chem Int Ed* 45(28):4681
49. Saueressig G, Crowley JN, Bergamaschi P, Bruhl C, Brenninkmeijer CAM, Fischer H (2001) *J Geophys Res Atmos* 106:23127
50. Schwarz H (2003) *Angew Chem Int Ed Engl* 42:4442
51. Wesendrup R, Schröder D, Schwarz H (1994) *Angew Chem Int Ed Engl* 33:1174
52. Pavlov M, Blomberg MRA, Siegbahn PEM, Wesendrup R, Heinemann C, Schwarz H (1997) *J Phys Chem* 101:1567
53. Wesendrup R, Schwarz H (1995) *Angew Chem Int Ed Engl* 34:2033
54. Sändig N, Koch W (1998) *Organometallics* 17:2344
55. Irigoas A, Elizade O, Silanes I, Fowler JE, Ugalde JM (2000) *J Am Chem Soc* 122: 114
56. Trage C, Schröder D, Schwarz H (2003) *Organometallics* 22:693, addendum (2003) 22:1348
57. Yumura T, Yoshizawa K (2001) *Organometallics* 20:1397
58. Fiedler A, Kretzschmar I, Schröder D, Schwarz H (1996) *J Am Chem Soc* 118:9941
59. Brönstrup M, Schröder D, Kretzschmar I, Schwarz H, Harvey JN (2001) *J Am Chem Soc* 123:142
60. Yumura T, Amenomori T, Kagawa Y, Yoshizawa K (2002) *J Phys Chem A* 106:621
61. Schröder D, Holthausen MC, Schwarz H (2004) *J Phys Chem B* 108:14407
62. Stöckigt D, Schwarz H (1994) *Chem Ber*, p 2499
63. Stöckigt D, Schwarz H (1995) *Liebigs Ann*, p 429
64. Brönstrup M, Schröder D, Schwarz H (1999) *Can J Chem* 77:774
65. Ryan MF, Stöckigt D, Schwarz H (1994) *J Am Chem Soc* 116:9565
66. Böhme DK, Schwarz H (2005) *Angew Chem Int Ed* 44:2336
67. Kappes MM, Staley RH (1981) *J Am Chem Soc* 103:1286
68. Buckner SW, Gord JR, Freiser BS (1988) *J Am Chem Soc* 110:6606
69. Schröder D, Schwarz H (1990) *Angew Chem Int Ed Engl* 29:1431
70. Balaj OP, Balteanu I, Rossteuscher TT, Beyer MK, Bondybey VE (2004) *Angew Chem Int Ed* 43:6519
71. Shi Y, Ervin KM (1998) *J Chem Phys* 108:1757
72. Blagojevic V, Jarvis MJY, Flaim E, Koyanagi GK, Lavrov VV, Bohme DK (2003) *Angew Chem Int Ed* 42:4923
73. Blagojevic V, Orlova G, Bohme DK (2005) *J Am Chem Soc* 127:3545
74. Water T, O'Hair RA, Wedd AG (2003) *J Am Chem Soc* 125:3384

75. Zemski KA, Justes DR, Castleman AW Jr (2002) *J Phys Chem B* 106:6136
76. Bell RC, Zemski KA, Kerns KP, Denkg HT, Castleman AW Jr (1998) *J Phys Chem A* 102:1733
77. Zemski KA, Justes DR, Castleman AW Jr (2001) *J Phys Chem A* 105:10237
78. Bell RC, Castleman AW Jr (2002) *J Phys Chem A* 106:9893
79. Justes DR, Moore NA, Castleman AW Jr (2004) *J Phys Chem B* 108:3855
80. Bell RC, Zemski KA, Castleman AW Jr (1998) *J Phys Chem A* 102:8293
81. Bell RC, Zemski KA, Castleman AW Jr (1999) *J Phys Chem A* 103:1585
82. Bell RC, Zemski KA, Castleman AW Jr (1999) *J Phys Chem A* 103:2992
83. Justes DR, Mitric R, Moore NA, Bonacic-Koutecky V, Castleman AW Jr (2003) *J Am Chem Soc* 125:6289
84. Feyel S, Schröder D, Schwarz H (2006) *J Phys Chem A* 110:2647
85. Cornehl HH, Heinemann C, Schröder D, Schwarz H (1995) *Organometallics* 14:992
86. Feyel S, Schröder D, Rozanska X, Sauer J, Schwarz H (2006) *Angew Chem Int Ed* 45(28):4677
87. Bernhardt TM (2005) *Int J Mass Spectrom* 243:1
88. Socaciu LD, Hagen J, Bernhardt TM, Wöste L, Heiz U, Häkkinen H, Landman U (2003) *J Am Chem Soc* 125:10437
89. Vann WD, Castleman AW Jr (1999) *J Phys Chem A* 103:847, and references cited therein
90. Jackson P, Harvey JN, Schröder D, Schwarz H (2001) *Int J Mass Spectrom* 204:233
91. Koszinowski K, Schlangen M, Schröder D, Schwarz H (2005) *Eur J Inorg Chem* 2464
92. Oliveira MC, Marcalo J, Vieira MC, Ferreira MAA (1999) *Int J Mass Spectrom* 185/186/187:825
93. Brümmer M, Kaposta C, Santambrogio G, Asmis KR (2003) *J Chem Phys* 119:12700
94. Asmis KR, Meijer G, Brümmer M, Kaposta C, Santambrogio G, Wöste L, Sauer J (2004) *J Chem Phys* 120:6461
95. Koyanagi GK, Bohme DK, Kretzschmar I, Schröder D, Schwarz H (2001) *J Phys Chem A* 105:4259
96. Gibson JK, Marcalo J (2006) *Coord Chem Rev* 250:776
97. Gehret O, Irion MP (1996) *Chem Eur J* 2:598
98. Engeser M, Weiske T, Schröder D, Schwarz H (2003) *J Phys Chem A* 107:2855
99. Koszinowski K, Schröder D, Schwarz H (2003) *J Phys Chem A* 107:4999
100. Schröder D, Engeser M, Brönstrup M, Daniel C, Spandl J, Hartl H (2003) *Int J Mass Spectrom* 228:743
101. Schröder D, Roithová J, Schwarz (2006) *Int J Mass Spectrom* (in press) published online 5 July 2006 (doi:10.1016/j.imjs.2006.05.024)
102. Khitrov GA, Strouse GF, Gaumet J-J (2004) *J Am Soc Mass Spectrom* 15:260
103. Schröder D, Schwarz H, Polarz S, Driess M (2005) *Phys Chem Chem Phys* 7:1049