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Gas-Phase Chemistry

Chemistry with Methane: Concepts Rather than Recipes

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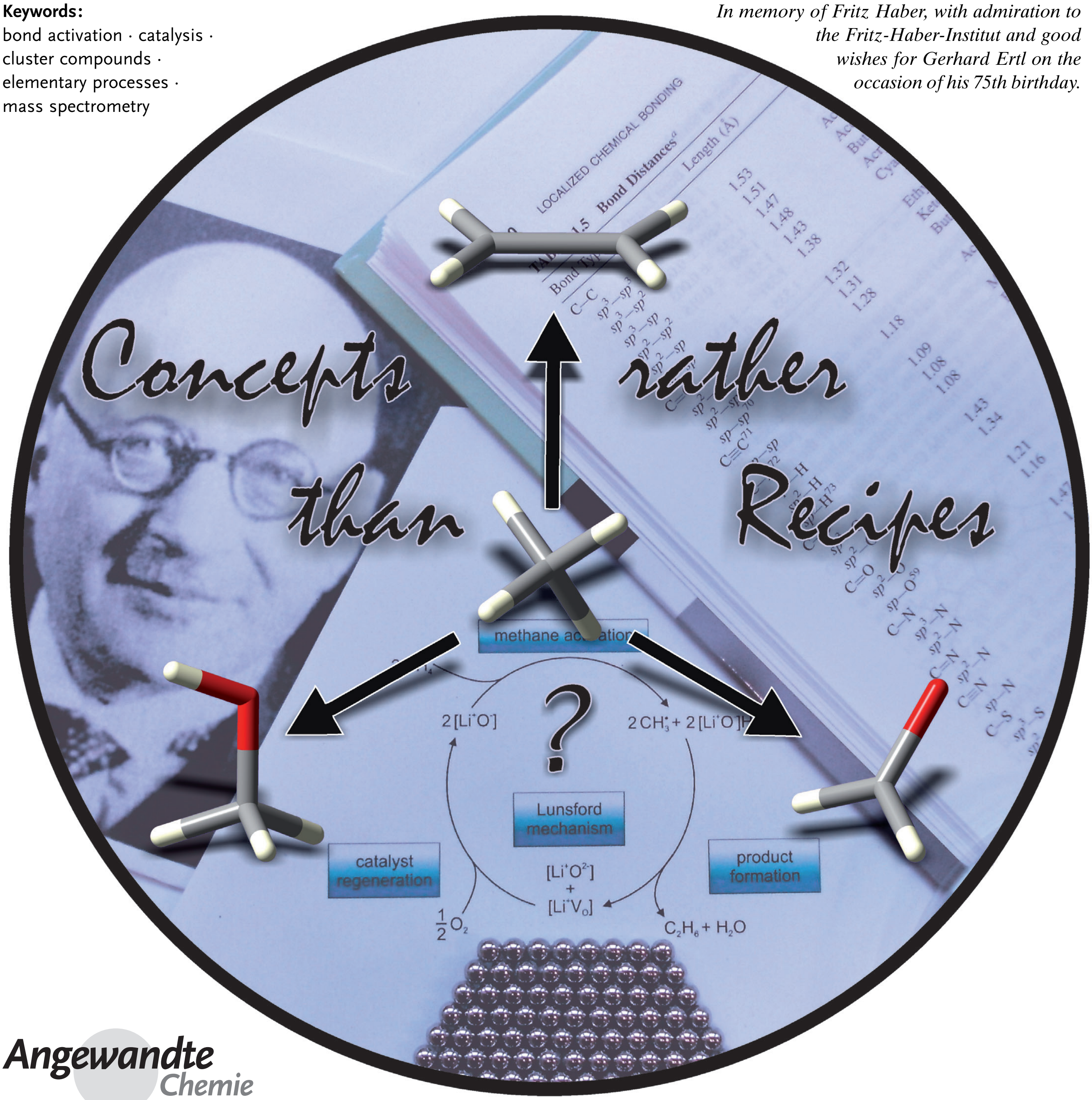
In memory of Fritz Haber, with admiration to the Fritz-Haber-Institut and good wishes for Gerhard Ertl on the occasion of his 75th birthday.



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Four seemingly simple transformations related to the chemistry of methane will be addressed from mechanistic and conceptual points of view: 1) metal-mediated dehydrogenation to form metal carbene complexes, 2) the hydrogen-atom abstraction step in the oxidative dimerization of methane, 3) the mechanisms of the $CH_4 \rightarrow CH_3OH$ conversion, and 4) the initial bond scission (C−H vs. O−H) as well as the rate-limiting step in the selective $CH_3OH \rightarrow CH_2O$ oxidation. State-of-the-art gas-phase experiments, in conjunction with electronic-structure calculations, permit identification of the elementary reactions at a molecular level and thus allow us to unravel detailed mechanistic aspects. Where appropriate, these results are compared with findings from related studies in solution or on surfaces.

From the Contents

1. Introduction

> “… I believe that in twenty-five years methane will be the most popular ligand in coordination chemistry.”
>
> Joseph Chatt, 1976[1]

While, in retrospect, Chatt’s bold prediction may be dismissed as exaggerated, there cannot possibly exist any serious doubt about the grand challenges associated with the activation and functionalization of methane.[2] For example, current large-scale, economically viable processes at ambient conditions are unable to bring about *direct* conversion of methane to methanol [Eq. (1)], to couple this alkane with

$$CH_4 + O_2 \rightarrow CH_3OH + \langle O \rangle \qquad (1)$$

carbon dioxide [Eq. (2)], or to use methane as a hydrogen

$$CH_4 + CO_2 \rightarrow CH_3CO_2H \qquad (2)$$

source to produce *directly* hydrogen peroxide or ammonia [Eq. (3) and (4)].

$$CH_4 + 3\,O_2 \rightarrow 2\,H_2O_2 + CO_2 \qquad (3)$$

$$3\,CH_4 + 3\,O_2 + 2\,N_2 \rightarrow 4\,NH_3 + 3\,CO_2 \qquad (4)$$

Clearly, a part of the difficulties is due to the intrinsic properties of the hydrocarbon, as indicated by the significant energies required for both homo- and heterolytic C−H bond cleavages, the negligibly small (if not negative) electron affinity, the large ionization energy, the huge HOMO–LUMO gap, the extremely high pK_a value, the absence of a dipole moment, and the rather small polarizability of CH_4. All these features make the substrate rather unsuitable for ordinary redox or acid–base chemistry. Moreover, in the context of CH_4 activation for the time being, tunable catalysts are not available to solve the deceptively simple problems of bond breaking and bond making or the coupling of the molecular fragments and the liberation of the product from the catalyst. Furthermore, attempts aimed at uncovering the elementary steps and elucidating mechanistic aspects associated with these transformations have proved particularly challenging.[2] This deplorable situation is not really surprising and is further enhanced given the enormous complexity that prevails in “real-life situation” in which often ill-defined effects of solvents, counterions, aggregates, or surface inhomogeneities obscure a reaction center or mask the intrinsic properties of a reactive intermediate. Clearly, a detailed understanding of the reaction mechanisms, derived from atomic or molecular-level insights, is desirable if not necessary for improving existing and designing new catalysts.[3]

Gas-phase studies on “isolated” reactants provide an ideal arena for probing experimentally the energetics and kinetics of a chemical reaction in an unperturbed environment at a strictly molecular level. In fact, in the last two decades numerous mass-spectrometry-based experiments have been exploited to provide insight into the elementary steps of various catalytic reactions and to characterize in detail reactive intermediates that have previously not been within the reach of conventional condensed-phase techniques.[4] Of course, as a result of the net Coulombic charge of the ions studied in high vacuum as well as the absence of counterions and solvation, these “naked” species will, in general, be much more reactive than their condensed-phase counterparts. Thus, gas-phase studies will, in principle, never account for the

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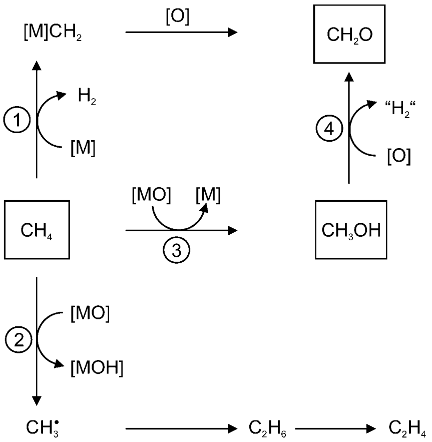
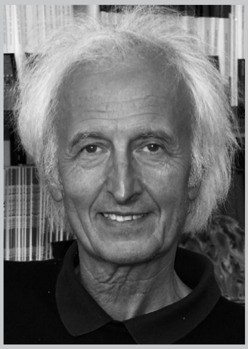
precise mechanisms, energetics, and kinetics which prevail in the condensed phase, and direct transfers of the conclusions arrived at are, in general, not warranted. Having said that, studies of this kind, performed under well-defined conditions and complemented by computational investigations, have nevertheless proved meaningful, for they provide a *conceptual* framework to analyze the reactions in question. In fact, the Degussa process, that is, the platinum-mediated coupling of CH_4 and NH_3 to generate HCN,[5a] may serve as a good example. Mass-spectrometry-based experiments[5b–d] suggested the key role of CH_2NH as a crucial transient, and the existence of this species was later confirmed by means of in situ photoionization studies.[5e]

In this Review, we focus our attention on four reactions, all of which are associated with the chemistry of methane (Scheme 1): metal-mediated dehydrogenation of methane, process ①, oxidative dimerization of methane (ODM), process ②, the methane→methanol conversion, process ③, and the selective oxidation of methanol to formaldehyde, process ④.



Scheme 1. Network for methane transformations. [M] stands for a metal (to be specified in the text) and [O] for any suitable oxidant.

While we will refrain from describing the various experimental techniques and computational methodologies (which are available from the references given), we will rather focus on the elucidation of the (often) intriguing mechanisms, and—where appropriate—a comparison will be made with related processes performed in the condensed phases.



Helmut Schwarz studied chemistry at the Technische Universität Berlin (TUB) from 1966–1971. After completing his Ph.D. in 1972 under the supervision of Ferdinand Bohlmann and his habilitation in 1974 (both at TUB), he spent some time abroad (ETH Zürich, Cambridge University, and MIT Cambridge) before he returned in 1978 to his alma mater to join the Institute of Chemistry. Dr. Schwarz has occupied visiting positions at 14 academic institutions worldwide and has delivered more than 900 invited or name lectures. Since January 2008 he has served as President of the Alexander von Humboldt-Stiftung.

2. Dehydrogenation of Methane: Relativistic and Cluster-Size Effects

> "*[Relativistic effects] are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions.*"
> Paul A. M. Dirac, 1929[6]

Dehydrogenation of methane (Scheme 1, process ①) to generate $[M]CH_2$ is of conceptual interest, as the methylene complex can serve as an intermediate in the metal-mediated conversion $CH_4 \rightarrow CH_2O$.[7] To make dehydrogenation thermochemically feasible, the metal–methylidene bond strength $D_0(M{-}CH_2)$ must exceed the heat of dehydrogenation of methane [Eq. (5)].

$$CH_4 \rightarrow CH_2 + H_2 \quad \Delta_rH = 111\ \text{kcal mol}^{-1} \tag{5}$$

Among "bare" transition-metal cations, this requirement is met only by some of the 5d elements, for example, $M^+ = Ta$, W, Os, Ir, and Pt.[8] In fact, in contrast to their lighter 3d and 4d congeners, these cations bring about spontaneous gas-phase dehydrogenation of methane at room temperature, as first reported by Irikura and Beauchamp[9] and later by others.[10] The remarkable increase in bond strength from, for example, 74 kcal mol^{-1} (for $Ni^+{-}CH_2$) to 111 kcal mol^{-1} (for $Pt^+{-}CH_2$)[11] has been attributed to a sizeable relativistic stabilization[12] of the 6s orbital of M^+ in these cationic complexes $M^+{-}CH_2$, as demonstrated for $M = Pt$ by fully relativistic, four-component Dirac–Fock–Coulomb benchmark calculations including correlation effects.[8,13] Actually, up to 40% of the bond strength in $Pt^+{-}CH_2$ is due to a relativistic contribution.[8,12,13b]

Armentrout and co-workers have extended the earlier work[9] and performed extensive experimental and computational studies for the systems M^+/CH_4 ($M = Re$,[11b] W,[14] Ir,[15] and Ta[16]). Most interesting is their finding that in the course of dehydrogenation, in particular to form the insertion intermediate $H{-}M^+{-}CH_3$, a spin–orbit-mediated switch from the high-spin ground state to the low-spin excited surface is crucial. As will be shown later in a different context, this scenario of a two-state reactivity (TSR) pattern,[17] in which excited states play a pivotal role, is a hallmark of many transition-metal-mediated processes.

TSR matters also in the unexpected thermal gas-phase dehydrogenation of CH_4 by main-group atomic As^+.[18] As shown in Figure 1, in the course of the reaction the ground-state triplet asymptote of the couple As^+ ($^3P_0$)/CH_4 undergoes a crossover to the excited singlet surface at a minimal-energy crossing point (MECP) located between the encounter complex **As-2** and the oxidative addition intermediate **As-3**. If the system stayed on the triplet ground-state surface, insurmountably high transition states (e.g. **As-TS$_{3-4}$** or **As-TS$_{4-5}$**) would have to be overcome. Instead, it is the very spin-

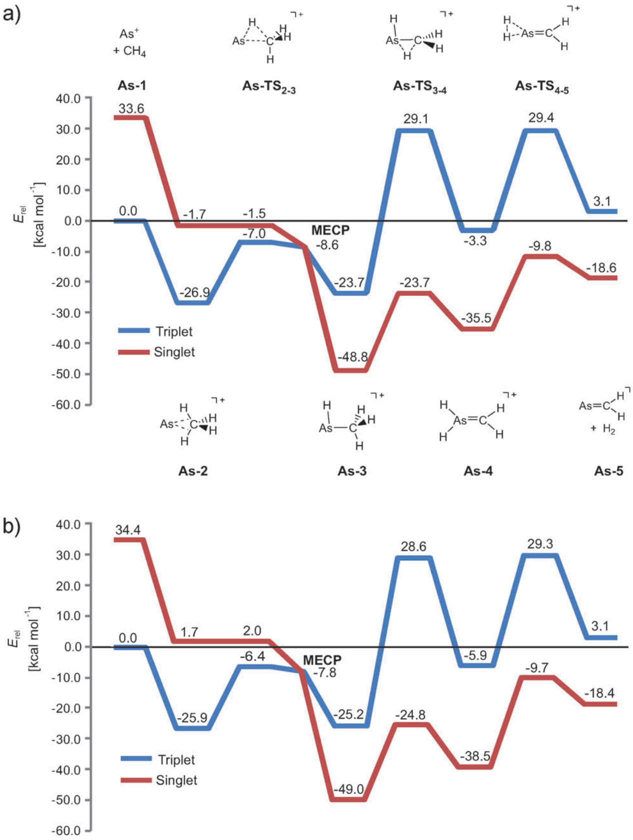


Figure 1. Potential-energy surfaces (PESs) for methane dehydrogenation with atomic As^+, calculated a) at the B3LYP/cc-pVTZ-DK level, including DKH2, and b) at the B3LYP/6-311++G** level without inclusion of relativistic effects (adapted from Ref. [18b]).

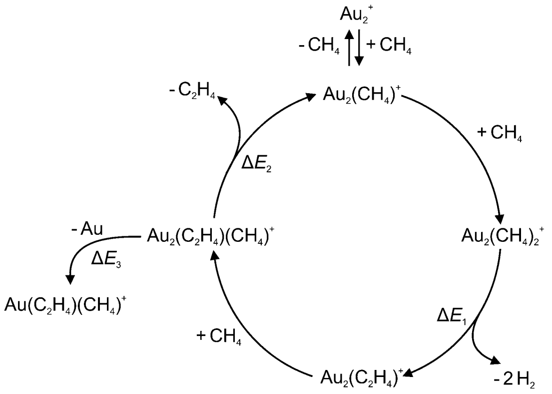
flip that opens up a reaction channel for a thermal process which would not be accessible at all for the reactants. Interestingly, as shown by a comparison of Figures 1a and b, scalar relativistic effects, however, do *not* affect the energetics in this particular system. Finally, in the thermal dehydrogenation of methane by the doubly-charged metal ion Ta^{2+}[19a] or the actinide species Th, Th^+, and Th^{2+},[19b–f] a TSR scenario has also been invoked.

Admittedly, bare metal cations have been rightly considered as extreme "reagents", and the findings derived from their reactions in the gas phase have little relevance to processes in solution or on surfaces—clearly, the reductionist principle in simplifying the complexity that prevails in reality has been stretched a bit too far. More appropriate models are clusters, and collections of cluster have been suggested as the reactive sites on surfaces.[20] In fact, size-selected unsupported neutral platinum clusters not only react with methane but also exhibit a remarkable size dependence in the dehydrogenation of CH_4, and the analysis reveals that coordinative unsaturation is of crucial importance.[21] A related behavior has also been observed for free charged $Pt_n^{+/-}$ clusters ($n = 1$–21) which, in addition to pronounced size effects, exhibit the following trends: 1) Cationic clusters, owing to their electrophilic character and to the mechanism of C–H bond activation, are generally more reactive than their anionic counterparts, with the reactivity of a given neutral platinum cluster falling between those of the charged systems; 2) with increasing cluster size the reactivity drops.[22] The anomalously low reactivity of Pt_4^+[22] has been traced back to the lack of a thermochemical driving force.[23c] In the room-temperature reactions of cationic heteronuclear MPt^+ (M = Cu, Ag, Au) or of the homonuclear Rh_2^+ clusters, dehydrogenation of CH_4 is also facile.[5c,d,23]

A notable cluster-size effect in the context of catalytic methane activation was reported by Bernhardt, Landman, and co-workers.[24] While atomic ground-state Au^+ ($^1S_0$) is entirely unreactive towards methane,[25] isolated Au_2^+ clusters mediate C–C coupling of methane at increased substrate pressure to yield ethane [Eq. (6)].

$$Au_2^+ + 2\,CH_4 \rightarrow Au_2^+ + C_2H_4 + 2\,H_2 \qquad (6)$$

In this experimental and computational study, approximately 10^6 mass-selected Au_2^+ ions were confined to an ion trap (which acts, so to speak, as the gas-phase chemist's test tube) for a few hundred microseconds in CH_4/He mixtures at a pressure of about 1 Pa and a temperature that was varied between 200 and 300 K. These experimental conditions permit derivation of the catalytic cycle depicted in Scheme 2, which was completely characterized in terms of the relevant thermodynamic and kinetic parameters. Several features are noteworthy. 1) Owing to the rather high pressure applied, reaction intermediates were collisionally stabilized and thus accessible; further, the temperature variation permitted the study of endothermic processes. 2) These findings illustrate an oxidative coupling of methane (OCM) at ambient temperature. 3) In the multicollision experiment, methane is not only involved as a reactant but also serves as a ligand to release C_2H_4 from the Au_2^+ catalyst. 4) Working at higher pressure removes the problem of the so-called "pressure gap" between the high vacuum and condensed phases, which often hampers model studies in their "relevance" for understanding real catalysis.[3b,26] As to some of the facets contained in Scheme 2, the first barrier ΔE_1, surpassed only at temperatures above 250 K, is encountered in the sequence of C–H bond activation, making an H–H bond, and the elimination of H_2. A second barrier (ΔE_2) must be



Scheme 2. Simplified representation of the catalytic cycle for C–C coupling of methane (adapted from Ref. [24]).

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involved in the release of C_2H_4 from the intermediate $Au_2(C_2H_4)(CH_4)^+$, because this intermediate is observed between 250 and 270 K, but not at 300 K. Finally, a third barrier (ΔE_3) is associated with the cluster degradation. As stated in a Highlight article,[27] these findings, in addition to their fundamental importance, are likely to be of practical importance in the design of catalysts.

Finally, it should be mentioned that coupling of methane to produce C_2H_4 has also been realized in a cluster-assisted σ-bond-activation reaction. Here, *atomic* Ti^+, at elevated CH_4 pressure, undergoes C–H bond activation and oxidative coupling of the CH_n ($n = 2, 3$) fragments in $Ti(CH_4)_m^+$ clusters ($m \geq 4$) at thermal energies.[28,29]

3. Hydrogen-Atom Abstraction from Methane: The Very First Step in the Lunsford Mechanism of Oxidative Coupling of Methane (OCM)

Much of the research on the direct conversion of methane has been devoted to this reaction, which involves the catalytic conversion of methane and oxygen to ethane and water [Eq. (7)] at elevated temperature (above 650 °C).[2d,30]

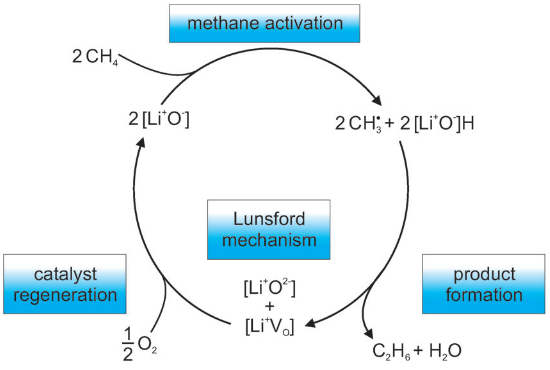
$$2\,CH_4 + {}^{1}\!/_{2}\,O_2 \rightarrow C_2H_6 + H_2O \qquad (7)$$

The fundamental aspects of the problem involve both a heterogeneous component, which includes the activation of CH_4 on (usually doped) metal oxide surfaces, and a homogeneous gas-phase part; in the latter, coupling of the free methyl radicals and subsequent dehydrogenation ($C_2H_6 \rightarrow C_2H_4$) occurs. Much of the current debate[31] centers around the nature of the active metal oxide surface species, which, according to Lunsford's suggestion,[30b,32] corresponds to an oxygen-centered radical (Scheme 3). However, no controversy exists as to the rate-limiting step of OCM, and the consensus view assigns this role to the initial homolytic scission of the C–H bond of methane.[33]

Perhaps the most compelling evidence for the role of oxygen-centered radicals in the hydrogen-atom abstraction step by metal oxides [Eq. (8)], as well as mechanistic insight

$$MO^{\bullet} + H{-}CH_3 \rightarrow MO{-}H + CH_3^{\bullet} \qquad (8)$$

into the elementary steps of the reaction with an emphasis on the detailed role of [M], have been provided by gas-phase studies of mass-selected, electronic ground-state metal oxide ions. These include not only the transition-metal-based oxides $OsO_4^{+\bullet}$,[9a] $FeO^{+\bullet}$,[34] $MnO^{+\bullet}$,[35] $MoO_3^{+\bullet}$,[36] $V_4O_{10}^{+\bullet}$,[37] $TiO_2^{+\bullet}$,[38] $ZrO_2^{+\bullet}$,[38] and their oligomeric clusters[39] but also main-group-element oxides, for example, $MgO^{+\bullet}$,[40] $MO^{+\bullet}$ (M = Ca, Sr, Ba),[41] $PbO^{+\bullet}$,[42] non-metallic $SO_2^{+\bullet}$,[43] mixed metal/nonmetal clusters $P_nV_{4-n}O_{10}^{+\bullet}$ ($n = 1, 2, 4$),[44] the bimetallic oxide $AlVO_4^{+\bullet}$,[45] as well as the oligomeric clusters $(Al_2O_3)_n^{+\bullet}$ ($n = 3$–5).[46] Common to all these systems are the following features: 1) A very efficient homolytic C–H bond activation according to Equation (8) achieved at room temperature; this activation is a consequence of a favorable thermochemistry, as the hydrogen affinities of these element oxide species exceed the C–H bond strength in methane, and 2) without exception, according to the theoretical studies, all element oxide radical ions exhibit high spin densities at a terminal oxygen atom.



Scheme 3. The Lunsford mechanism[32] for the oxidative coupling of methane (adapted from Ref. [31b]).

The crucial role of an oxygen-centered radical is demonstrated by the following experimental observations and computational findings. 1) For the oligomeric clusters $(Al_2O_3)_n^{+\bullet}$ ($n = 3$–5) only those clusters react spontaneously at room temperature according to Equation (8) that have an even number of aluminum atoms ($Al_6O_9^{+\bullet}$, $Al_8O_{12}^{+\bullet}$, and $Al_{10}O_{15}^{+\bullet}$); clusters that contain an odd number of aluminum atoms ($Al_7O_n^+$ ($n = 9, 10, 11$) and $Al_9O_n^+$ ($n = 13, 14$)) lack a radical center and do not exhibit any reactivity towards CH_4.[46] 2) In contrast to the open-shell cluster $Al_3VO_7^{+\bullet}$, whose spin is not located at a terminal oxygen atom, the related system $AlVO_4^{+\bullet}$ brings about efficient homolytic cleavage of the C–H bond of CH_4 at room temperature. DFT calculations indicate that the hydrogen-atom transfer is exclusively confined to the terminal Al–O and not the V–O unit, as it is the former group at which the spin is located (Figure 2).[45a] Similarly, in the mixed $P_nV_{4-n}O_{10}^{+\bullet}$ clusters ($n = 1, 2$) or the heteronuclear vanadium silicon oxide radical cation clusters, the radical site is located at the terminal P–O or Si–O units.[44b,c,45b] 3) Finally, while H-atom abstraction from the closed-shell system CaO/CH_4 is calculated to be slightly exothermic, the barrier of the process is insurmountably high;[47] this behavior very much contrasts with that of the rather reactive $CaO^{+\bullet}/CH_4$ couple.[41]

As to the mechanism(s) of the hydrogen-atom abstraction from CH_4, two conceivable scenarios have been identified, that is, a direct pathway ("harpoon" mechanism) and an indirect process in which the hydrogen delivery from the

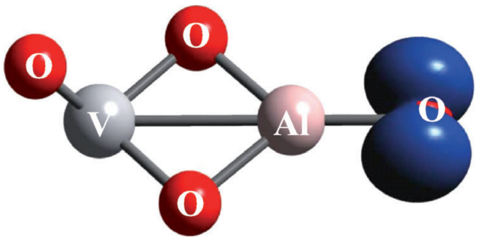


Figure 2. Calculated spin-density distribution (in blue) for the optimized ground-state structure of $AlVO_4^{+\bullet}$ (adapted from Ref. [45a]).

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carbon atom to the oxygen atom is mediated by the metal atom. Convincing examples for both scenarios are known, with $SO_2^{+\cdot}$, $AlVO_4^{+\cdot}$, and $P_nV_{4-n}O_{10}^{+\cdot}$ ($n = 0, 1, 2, 4$) belonging to the former and $MgO^{+\cdot}$, $PbO^{+\cdot}$, $MnO^{+\cdot}$, $FeO^{+\cdot}$, and $MoO_3^{+\cdot}$ to the latter. Both mechanistic variants will be presented below.

In the gas-phase reaction of the polynuclear oxide cluster $V_4O_{10}^{+\cdot}$ with methane,[48] no long-lived encounter complex $V_4O_{10}^{+\cdot}/CH_4$ seems to exist; rather, in a barrier-free process (Figure 3) the hydrogen atom is pulled away to produce, in a rather exothermic reaction, the intermediate $[V_4O_9OH]^+\cdots CH_3^\cdot$, from which the loosely bound $CH_3^\cdot$ is liberated.[37]

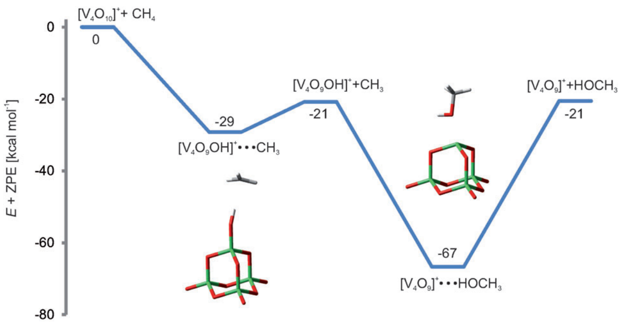

Figure 3. Energy diagram for the reaction of $V_4O_{10}^{+\cdot}$ and methane calculated at the B3LYP/TZVP level. The values (in kcal mol^{-1}) are given relative to the entrance channel and are corrected for zero-point energy (adapted from Ref. [37]).

The evolution of this efficient process (60 % of the collision rate), which is associated with an intramolecular kinetic isotope effect (KIE) of 1.35,[37,49] has been confirmed by molecular dynamics (MD) simulations (Figure 4 and Figure 5). For the first 450 fs of the simulation, the potential energy decreases steadily, driven only by the small attractive forces between methane and the cluster ion, which is indicative of a barrier-free reaction. In parallel, the O−H and V−C distances decrease steadily, and the C−H distance increases. After 450 fs, when the system has gained approximately 24.5 kcal mol^{-1} internal energy, energy is transferred into the C−H and O−H stretching modes, corresponding to oscillations of the hydrogen atom between the vanadyl oxygen atom and the methyl carbon atom. Further, the V−C distance decreases until $t = 470$ fs and then slowly increases again, thus indicating the beginning of the expulsion of the CH_3 radical.

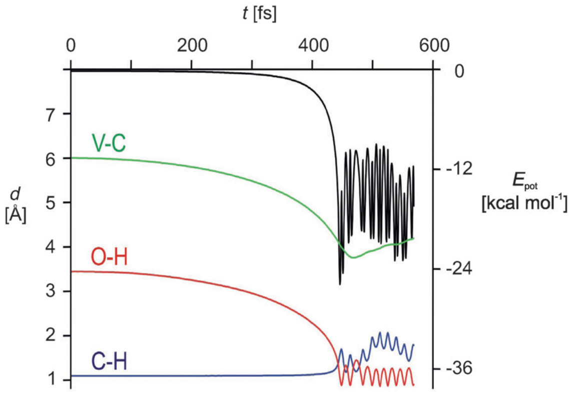

Figure 4. Evolution of the potential energy and bond lengths in the MD simulation of the reaction of $V_4O_{10}^{+\cdot}$ and methane. The energy is shown in black, d(C−H) in blue, d(O−H) in red, and d(V−C) in green. The fluctuations after 450 fs result from vibrational motions, mainly of the OH group (adapted from Ref. [37]).

The progress of the reaction can also be seen by inspection of the calculated spin densities shown in Figure 5. In the initial-state structure (a), the spin density is similar to that of the isolated $V_4O_{10}^{+\cdot}$ cluster and only insignificantly more delocalized. Structure (b) describes the situation after 443 fs; the O−H and C−H distances are nearly identical, and the spin density is distributed between the vanadyl oxygen atom and the carbon atom and is polarized along the O-H-C axis. Finally, in the product (c), the spin is completely transferred to the methyl radical.

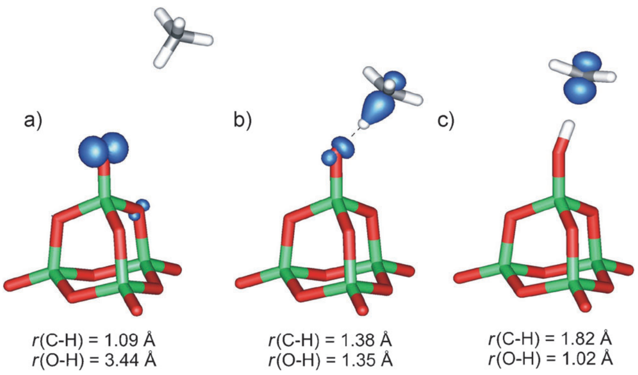

Figure 5. Calculated spin densities for the reaction of $V_4O_{10}^{+\cdot}$ and methane after a) 0 fs and b) 443 fs. c) Calculated spin density of the optimized product structure. C−H and O−H distances are given below the structures (adapted from Ref. [37]).

Room-temperature activation of CH_4 by diatomic $MgO^{+\cdot}$ may serve as an example for a “metal-mediated” hydrogen abstraction; such homolytic bond cleavage is also a hallmark of the reactions of CH_4 with $PbO^{+\cdot}$, $MnO^{+\cdot}$, $FeO^{+\cdot}$, and $MoO_3^{+\cdot}$ As shown in Figure 6, the reaction commences with the generation of an encounter complex $CH_4\cdots Mg^{2+}\cdots O^{-\cdot}$ in which the spin is almost exclusively located at the oxygen atom. Next, the methane molecule migrates around the magnesium atom toward the oxygen atom, delivery of a hydrogen atom occurs, and the newly formed methyl group is pulled back to the magnesium core. The thus formed $H_3C\cdots Mg^+{-}OH$ intermediate represents a complex between a loosely bound methyl radical, which carries more than 98 % of the spin, and protonated magnesium oxide. From this intermediate, $CH_3^\cdot$ is liberated in an entropy-driven dissociation; formation of the thermochemically more favored product combination $Mg^{+\cdot}/CH_3OH$ by a rebound mechanism is kinetically less attractive.[40]

Finally, in the context of homolytic C−H bond cleavage reactions, a brief comment seems befitting about using kinetic

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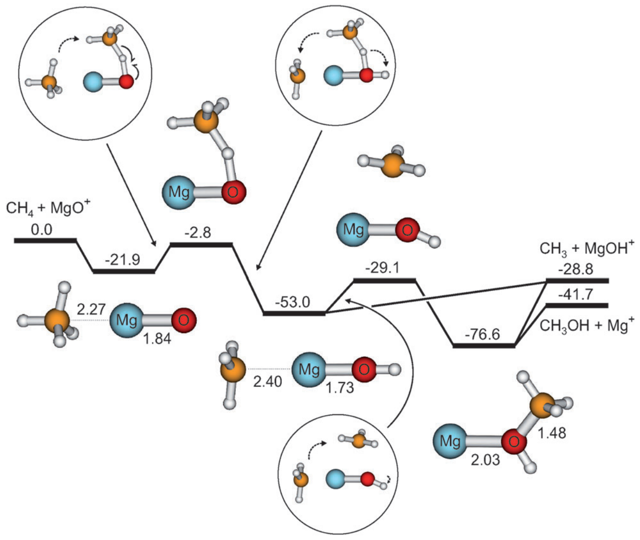

Figure 6. Potential-energy surface (in kcal mol^{-1}) for the reaction of MgO$^{+\cdot}$ with CH$_4$ calculated at the MP2/6-311+G(2d,2p) level of theory; selected bond lengths are given in Å. The encircled structures depict the rearrangements occurring along the reaction coordinate (adapted from Ref. [40]).

isotope effects as an experimental probe to classify reaction mechanisms. As already mentioned, direct hydrogen abstraction from CH$_4$ is characterized by rather small KIEs, whereas those homolytic C–H bond cleavages which are mediated by the metal core exhibit larger KIEs, typically greater than 2.0. Moreover, as discussed by Schröder et al. in detail,[50] for a given reaction type there exists a relationship between the size of the KIEs and the overall rate coefficients of the hydrogen-atom abstraction from methane. For example, the intermolecular KIE, derived from the reactions with CH$_4$ and CD$_4$, continuously increases from about 1.3 for MgO$^{+\cdot}$ via 2.1 and 2.4 for CaO$^{+\cdot}$ and SrO$^{+\cdot}$, respectively, to 3.2 for BaO$^{+\cdot}$.[41] This trend of increasing KIEs is paralleled by a decrease of the overall rate coefficients for the activation of methane, for example, from 3.9×10^{-10} for MgO$^{+\cdot}$ and 2.9×10^{-10} for CaO$^{+\cdot}$ to 9.8×10^{-11} and 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} for SrO$^{+\cdot}$ and BaO$^{+\cdot}$, respectively.[41,50] With regard to catalysis, this observation implies that the less reactive oxidants exhibit higher selectivities in terms of the associated KIEs, apparently in line with the time-honored Bell–Evans–Polanyi principle.[51]

4. The Conversion of Methane to Methanol: A Long-Time Conundrum Resolved at Long Last by the Two-State Reactivity Concept

> “*Dem Anwenden muss das Erkennen vorausgehen.*”
> Max Planck, 1919[52][*]

Planck’s comment on the decision to award the Nobel Prize for Chemistry (1918) to Fritz Haber, and repeated at the annual meeting of the Kaiser-Wilhelm-Gesellschaft on October 29, 1919 in a different context, does not only serve to this very day as a precept of Germany’s Max-Planck-Gesellschaft but also summarizes Haber’s exceptional skill in bridging the gap in the natural sciences between theory and application. In Bernal’s words, Haber was “the greatest authority in the world on the relations between science and industry”.[53]

Perhaps the largest potential for a major advance in methane conversion technology is in the discovery of a *direct* route to the formation of methanol and formaldehyde at ambient conditions,[2] and it is not unjustified to relate Sir Derek Barton’s famous dictum[2a] about “Holy Grails in Chemistry”[54] to the oxygenation of C–H bonds in alkanes, for example, the reaction in Equation (1), given the complexity of this deceptively trivial reaction, which looks easy only on paper.[55,56] In reality, there are quite a few challenges, as for example:

1) the *unbalanced stoichiometry*: there is one oxygen atom too many in Equation (1);
2) the *overoxidation challenge*: both intermediates CH$_3$OH and CH$_2$O are kinetically more prone to further oxidation than the starting molecule CH$_4$ with its thermochemically strong and kinetically inert C–H bond;
3) the *spin dilemma*: since CH$_4$ and CH$_3$OH possess singlet ground states, the reaction is spin-forbidden when O$_2$ is used as terminal oxidant.

Nature has solved these riddles in the evolutionary development of the methane monooxygenase (MMO) enzyme, which contains at the reaction center a structurally relatively simple, doubly oxygen-bridged diiron cluster.[57] MMO has served chemists as an enticing example of what could possibly be achieved, and FePO$_4$ is an interesting in vitro model for the production of CH$_3$OH and CH$_2$O when H$_2$ is added to CH$_4$ and O$_2$.[58] The two oxidation products are formed with selectivities of 23 and 45 %, respectively, but only at a disappointingly low methane conversion level of about 0.6 %. Similarly unsatisfying with regard to a large-scale, economically attractive, environmentally benign functionalization of CH$_4$ were the mechanistically appealing experiments of Periana et al., which made use of bipyrimidyl-substituted platinum(II) complexes,[2i,59a] in analogy to Shilov’s seminal studies employing platinum compounds dating back to the mid-20th century,[60] or Au^0-based oxidations of CH$_4$ with H$_2$SeO$_4$.[59b] With regard to practical applications, however, experiments which employ platinum-based solid catalysts are more promising.[59c,d]

A rewarding insight into the mechanisms—and thus the underlying obstacles encountered in the numerous, often frustrating solution-phase and surface-based experiments—has been derived in the last two decades from a happy marriage between sophisticated gas-phase experiments of mass-selected, electronic-ground-state metal oxide cations MO$^+$ and computational studies. Only some of the more fundamental aspects from this rather extensive work[61] will be addressed here. First, it should be mentioned in passing, without discussing this fascinating topic in any further detail, that the understanding of the simple gas-phase reaction, depicted in Equation (9a), has later proved helpful in the clarification and elucidation of the mechanisms of the intricate cytochrome P450 mediated hydroxylation of hydro-

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[*] “Knowledge ought to precede application.”

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$$\mathrm{MO^+ + CH_4} \longrightarrow \begin{cases} \mathrm{M^+ + CH_3OH} & (9a) \\ \mathrm{M(OH)^+ + CH_3^{\bullet}} & (9b) \\ \mathrm{M(CH_2)^+ + H_2O} & (9c) \end{cases}$$

carbons as well as in providing a rationale for the competitive H-atom abstraction versus O-atom transfer of nonheme iron(IV) oxide oxidants.[62]

In the stoichiometric gas-phase model reactions of MO^+ with CH_4, three principal product channels are conceivable [Eq. (9)], and the experimentally determined rate coefficients and branching ratios are controlled by thermochemical and spin considerations; Reaction (9c) is usually reserved for oxides that contain 5d metals.[7] In this Section, we will focus on features that are of particular relevance for the reaction shown in Equation (9a), in which the insertion intermediate $H_3C{-}M^+{-}OH$ is key. Although the metal has the formal oxidation state M^{III} in both MO^+ and $H_3C{-}M^+{-}OH$, there are fundamental differences in the bonding situations, which have important consequences. Thus, 3d and 4d metals cannot effectively support π-type double bonds in MO^+, which consequently leads to high-spin ground states for the MO^+ monocations. In contrast, the insertion intermediates primarily involve σ-type bonding, for which perfect pairing and thus low-spin ground states are preferred. Therefore, a situation results, in which the spin surfaces cross each other such that the reaction pathway of lowest energy demand must involve a crossover from the high-spin to the low-spin surface and eventually back to high spin in the final products. In fact, the analysis of the reactions of bare metal oxide cations in the gas phase led, among other things, to the development of the paradigm of two-state reactivity (TSR).[17c,d,62,63] The TSR scenario is now widely accepted in various areas of science far beyond gas-phase-ion chemistry, for example in organometallic chemistry[64] and also in the context of metalloenzymes.[62]

The (simplified) potential-energy surface for the reaction of bare FeO^+ with CH_4 (Figure 7) may serve as an illustrative example. After having formed an encounter complex $(CH_4)FeO^+$, spin–orbit-mediated coupling brings about a switch from the high-spin sextet ground state to an excited quartet state;[34e,65] only in this spin state is formation of the insertion intermediate $H_3C{-}Fe^+{-}OH$ via TS1 thermochemically possible under ambient conditions, and it is the spin change that avoids the high-energy TS1 on the ground-state sextet surface.

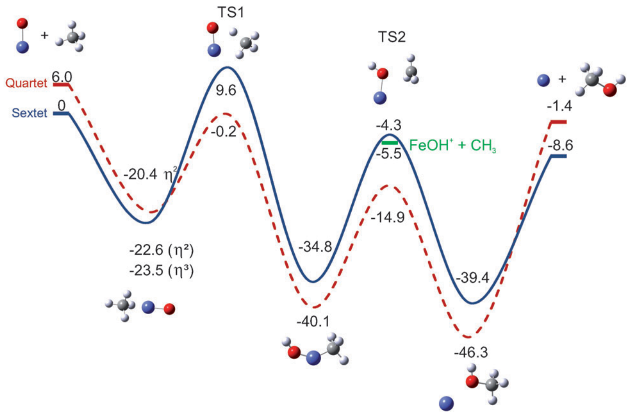

Figure 7. Schematic potential-energy surface for the reaction $FeO^+ + CH_4 \rightarrow Fe^+ + CH_3OH$. Relative energies (kcal mol^{-1}) are calculated at the CBS-QB3 level of theory (adapted from Ref. [34d]).

Thus, as stated above, excited states are involved in a thermal reaction. As pointed out by Poli and Harvey,[64a] it is only because of a spin change that these reactions occur at all under ambient conditions. The essence of the idea of a TSR scenario is depicted in Figure 8, and it represents the key element of “spin catalysis”: *a (thermal) reaction is accelerated by a spin change which, by avoiding energetically less attractive transition structures, opens up favorable pathways.*

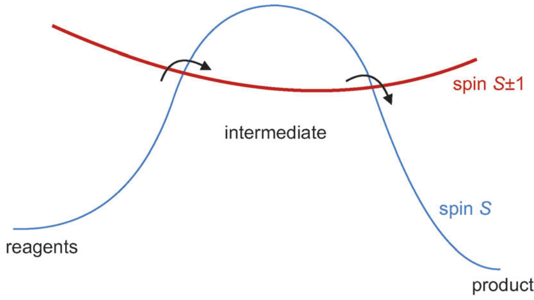

Figure 8. Qualitative energy profile for a spin-change-accelerated reaction (adapted from Ref. [64a]).

While the details of the PESs for C–H bond oxygenation by MO^+ depend very much on the nature of the transition metal M in MO^+, excellent agreement has been arrived at for the thermal reactions of MO^+ (M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) with CH_4 when compared with computational studies.[4a,34a,b,35a,b,66] Several notable, general trends are as follows: First, the early 3d transition-metal oxides ScO^+, TiO^+, VO^+, CrO^+, and MnO^+ have low-spin ground states. This characteristic alters the PESs such that the intersystem crossing does not occur in the vicinity of TS1 (Figure 7) but instead closer to TS2. As the ground states of the products are high-spin systems, only one spin flip is necessary. Next, the reactions of ScO^+, TiO^+, and VO^+ with CH_4 to produce CH_3OH are endothermic owing to the enormous $D_0(M^+{-}O)$ values (greater than 135 kcal mol^{-1}), which substantially exceed the oxygen-atom affinity of CH_4 to produce CH_3OH (90.7 kcal mol^{-1}). Further, as the O-atom transfer from CrO^+ is only slightly exothermic, none of these oxides bring about thermal activation of CH_4.

For MnO^+, the exothermicity of its reaction with methane already suffices to break the C–H bond and to generate $H_3C{-}Mn^+{-}OH$; next, this intermediate liberates a methyl radical in a spin-allowed, entropically favored process; the spin-forbidden rebound step, with subsequent CH_3OH loss, is not competitive. The two late-transition-metal oxides CoO^+ and NiO^+, when treated with CH_4, undergo spin inversion close to the entrance channel; an additional spin flip at the elimination of CH_3OH is not required, because the ground state of the resulting metal ions is of the $3d^n$ configuration. The

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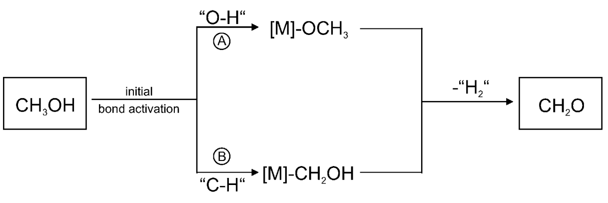
experimentally observed significant differences in the reaction coefficients (more than a factor of 20 in favor of NiO^+) in generating CH_3OH from CH_4 and MO^+ ($M = Co, Ni$) are due to details of the PESs close to the insertion step as well as to different spin–orbit coupling factors. Finally, according to the calculations, CuO^+ is predicted to be one of the most powerful hydrocarbon oxidants among all binary 3d metal oxide cations; however, as a consequence of its small bond-dissociation energy, $D_0(Cu^+{-}O) = 37.4\,kcal\,mol^{-1}$, to date all attempts to generate the reagent in the gas phase and to subject it to the stoichiometric or catalytic conversions of methane have failed. [See however the Addendum.]

The genuine gas-phase catalytic oxidation $CH_4 \rightarrow CH_3OH$ by MO^+ was realized quite some time ago for FeO^+[34a] and, more recently, for NiO^+ and PdO^+.[67] On the basis of computational and experimental studies, it was shown that NiO^+, owing to its easy availability and high selectivity, is a rather promising candidate, and experiments that use NiO- or FeO-doped zeolites as catalyst for the oxygenation of CH_4 under ambient conditions are also encouraged by computational and (for iron and copper) experimental investigations.[68]

5. On the Detailed Mechanisms of $CH_3OH \rightarrow CH_2O$ Oxidation

While most of the roughly 40 million metric tons of methanol processed annually are converted into a variety of diverse chemical products,[2k] the leading among them is formaldehyde, which is also one of the top 25 chemicals produced worldwide.[2k,69] Here, we focus on some mechanistic aspects of the conversion $CH_3OH \rightarrow CH_2O$, and the relevant questions in this context center around the following topics: 1) In the initial step (Scheme 4) does a metal-based mediator [M] preferentially induce a cleavage of the stronger O–H bond ($102.4\,kcal\,mol^{-1}$) or the weaker C–H bond ($91.7\,kcal\,mol^{-1}$), and 2) for a given sequence of events, which of the two hydrogen-transfer steps constitutes the rate-determining one? These questions will be addressed first by describing reactions of methanol with neutral atoms under matrix-isolation conditions, on surfaces, or in the gas phase when treated with bare or ligated ions. Subsequently, examples of genuine gas-phase catalysis will be presented, and, finally, a brief comparison will be made between model systems and a real catalyst.



Scheme 4. Pathways for a metal-mediated methanol–formaldehyde conversion.

5.1. The Initial Step: Cleavage of the Strong O–H versus the Weaker C–H Bond

In all matrix-isolation studies, often complemented by computational exercises, for the reactions of methanol with neutral atoms ($M = Fe$,[70] Si,[71] B,[72] Be,[73] Mg,[73a] Sc,[74] Ti,[75] or Mn[70a]) upon annealing or photochemical activation, the encounter complexes $M(CH_3OH)$ undergo, in a kinetically controlled fashion, specific activation of the stronger O–H bond (path Ⓐ Scheme 4) to produce the corresponding $[M]{-}OCH_3$ species.[76] Similarly, the numerous experimental investigations, employing the whole arsenal of contemporary advanced surface-spectroscopy techniques, combined with elaborate computational studies of the reactions of methanol on supported metal oxides, demonstrate that the "methoxide pathway" Ⓐ is preferred.[77] These studies, which, among other things, also deal with the role of support effects, formal oxidation states of the metal oxides, and selectivity effects caused by the atomic structures of the surfaces, further reveal that in the sequence $CH_3OH \rightarrow [M]OCH_3 \rightarrow CH_2O$ the second step, that is, the C–H bond activation in the methoxy intermediate, constitutes the rate-limiting one.[77] In a rather detailed computational investigation, the kinetic and mechanistic aspects of the $CH_3OH \rightarrow CH_2O$ conversion using titania-supported vanadates were addressed, and the following main conclusions were drawn:[78]

1) Methoxy species are key intermediates in the reaction, with a tetrahedral vanadia unit containing a vanadyl group, a methoxy group, and two bridging V-O-Ti sites forming the most stable one. A fivefold-coordinated vanadia unit was found to be potentially interesting for catalytic reactivity.
2) The rate-limiting step in the oxidation mechanisms corresponds to the transfer of a hydrogen atom from the $[V]{-}OCH_3$ intermediate to the catalyst oxygen site V=O (barrier of $41.0\,kcal\,mol^{-1}$) or to a bridging interface unit V-O-Ti (barrier $46.0\,kcal\,mol^{-1}$). Both pathways involve spin crossings from the singlet to the triplet potential-energy surfaces, involving TSR scenarios.

However, and perhaps not entirely unexpectedly, a change in mechanism can occur when methanol oxidation is brought about by oxide-*free* surfaces. For example, in the oxidative CH_3OH decomposition on Pt(111), according to periodic, self-consistent DFT calculations, the rate-limiting step is now assigned to initial O–H bond activation to produce a methoxy-bound intermediate.[79] Other computational work[80] arrived at the conclusion that C–H bond scission contributes to the first and rate-limiting step in the Pt(111) decomposition of CH_3OH; while this process is favored by $12\,kcal\,mol^{-1}$ as compared with an initial O–H bond activation (Figure 9),[80a] neither decomposition route for methanol can compete with the desorption of the intact substrate from the surface.

A change in mechanism has also been noted in the electrochemical decomposition of CH_3OH on platinum surfaces; a KIE of 3 for the system CH_3OH/CD_3OH and its absence for the CH_3OH/CH_3OD couple, together with other data, were interpreted in favor of the "hydroxymethyl

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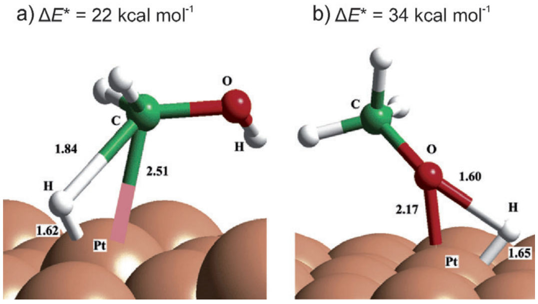


Figure 9. Transition structures calculated by DFT for a) C–H and b) O–H bond activation of methanol on Pt(111); selected bond lengths are given in Å (adapted from Ref. [80a]).

pathway" (Ⓑ in Scheme 4).[80,81] Finally, initial C–H rather than O–H bond cleavage is computationally predicted to be favored in methanol activation on sub-nanometer Pd clusters.[82]

Numerous gas-phase experiments with both cationic and anionic reagents, bare or ligated atoms, and clusters of different sizes and varying stoichiometries have been conducted over the last three decades and aimed at revealing the mechanisms of $CH_3OH \rightarrow CH_2O$ conversion at a strictly molecular level. While highly remarkable cluster-size effects,[83g–k,n,q] the role of formal oxidation states,[83q] or anomalously large kinetic isotope effects have been observed,[83e] most of these studies[83] did not provide a clear-cut mechanistic distinction between initial O–H versus C–H bond scission (Scheme 4). Preferred O–H bond activation, however, is suggested for the system FeO^+/CH_3OH according to experimental data[84a] and supported by DFT calculations.[84b] Similarly, mass-selected cations FeX^+ (X = OH, F) undergo a clean reaction with CD_3OH [Eq. (10)],[85a] while

$$FeX^+ + CD_3OH \rightarrow Fe(OCD_3)^+ + HX \qquad (10)$$

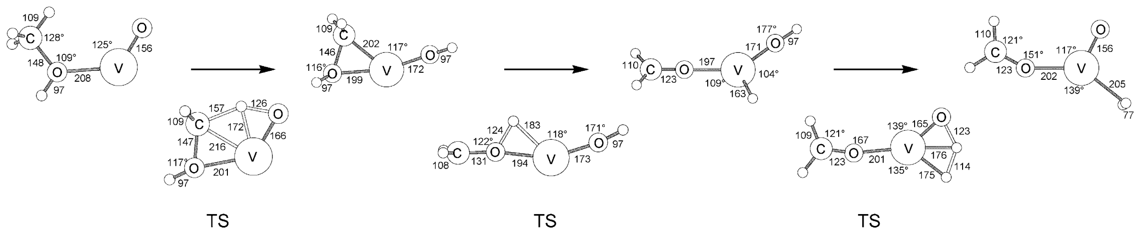
the related NiX^+ systems (X = OH, F, Cl, Br) effect both O–H and C–D bond activation of CD_3OH; the branching ratio is strongly ligand-dependent.[85b] For example, $Ni(OH)^+$ prefers O–H bond activation, but the complex $NiBr^+$ preferentially activates the C–D bond of CD_3OH.[85b] Finally, in the initial phase of the reaction of VO_3^- with methanol, extensive labeling experiments and computational studies indicate that specific activation of the O–H group prevails as well.[86]

Unambiguous examples for an initial C–H bond activation are rather scarce; for example, the gas-phase reaction between $Mn(CO)_3^-$ and methanol commences with the rate-limiting C–H bond cleavage of the substrate,[86a] and in the reaction of Co_n^+ ($n = 4, 5$) cluster ions with CD_3OH, only D_2 is liberated.[86b] For the oxidation of methanol by ferrate (FeO_4^{2-}), numerous pathways were considered computationally, and it appears that C–H and O–H bond scissions compete with each other.[87] This prediction, including computed KIEs to distinguish between different mechanistic scenarios, calls for an experimental verification. For the dehydrogenation of CH_3OH by mononuclear vanadium oxide cations, in line with the experimental findings, calculations clearly favor a reaction path that is initiated by activation of a C–H bond in the course of which the metal's oxidation state does not change (Scheme 5); moreover, spin changes from the ground-state triplet surface to the excited singlet manifold do not matter in this particular system, as the two electronic ground states are well-separated energetically and do not cross.[88]

The mechanisms of the $CH_3OH \rightarrow CH_2O$ oxidation by the Fenton reagent were studied by Baerends and co-workers at the DFT level[89] both in the gas phase by considering microsolvated clusters and in aqueous solutions. Two competing mechanisms were identified, in line with the dual nature of the reagent: 1) A direct one in which the high-valent $Fe^{IV}O^{2+}$ moiety homolytically abstracts a hydrogen atom from the methyl group (path Ⓑ in Scheme 4) and 2) a coordination mechanism in which after complexation the O–H bond of the substrate is cleaved heterolytically to generate initially an $Fe(OCH_3)$ species (path Ⓐ in Scheme 4). As expected, given the nature of highly charged systems, solvent effects matter, with the consequence that the energy barriers calculated are quite sensitive to changes of the microenvironment.[89]

A strongly metal-dependent, alternating activation of C–H versus O–H bonds of methanol occurs when the gas-phase species are generated upon electrospray ionization of methanolic solutions of MX_2 (M = Fe, Co, Ni; X = Br, I).[90–92] As shown in Figure 10, in the iron system selective activation of the hydroxy group of the ESI solvent prevails; in contrast, nickel salts activate the C–H bond, and for the cobalt complexes an intermediate situation is encountered.[90a]

Combining the labeling data (Figure 10) with structure-specific collision experiments of the $[M,C,H_3,O]^+$ product ions provides evidence for the exclusive formation of $Fe(OCH_3)^+$, $Ni(CH_2OH)^+$, and a mixture of $Co(OCH_3)^+$ and $Co(CH_2OH)^+$ with a preference for the methoxy complex.[90a]



Scheme 5. Computationally suggested pathway and relevant geometric data (bond lengths in pm) for the triplet species involved in the reaction of VO^+ with CH_3OH (adapted from Ref. [88]).

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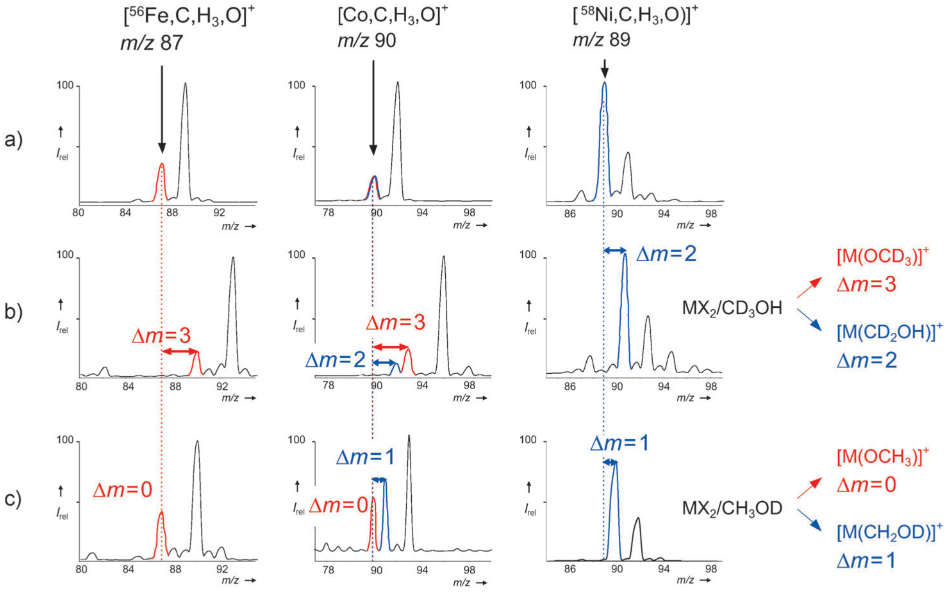

Figure 10. Partial ESI source spectra of the Fe, Co, and Ni halides MX_2 (X = Br, I) dissolved in a) CH_3OH/H_2O, b) CD_3OH/H_2O, and c) CH_3OD/D_2O (adapted from Ref. [90a]).

Interestingly, a mixture of $Rh(OCH_3)$ and $Rh(CH_2OH)$, with comparable Rh−O and Rh−C bond dissociation energies, has also been obtained from treating rhodium(I) porphyrines with methanol.[90b]

Mechanistic insight into the origin of the bond-selective, metal-dependent CH_3OH activation has been gathered from extensive DFT calculations and by experimentally establishing the precursors from which the $[M,C,H_3,O]^+$ species originate upon ESI of MX_2/CH_3OH solutions.[90a,92] For iron, the $Fe(OCH_3)^+$ product is due to sequential evaporation of up to eight CH_3OH molecules from $Fe(OCH_3)(CH_3OH)_n^+$ ($n \leq 8$), and the latter is generated by solvolysis of FeX_2 by the nucleophilic CH_3OH solvent. Moreover, high-spin $Fe(OCH_3)^+$ is, according to DFT calculations, 16.6 kcal mol^{-1} more stable than the quintet isomer $Fe(CH_2OH)^+$. For the co-generation of isomeric $[Co,C,H_3,O]^+$, two pathways have been identified. One, leading to the methoxy complex $Co(OCH_3)^+$, is analogous to that for the iron system starting from $Co(OCH_3)(CH_3OH)_n^+$ ($n \leq 8$). However, this precursor, in competition with sequential CH_3OH evaporation, also undergoes loss of CH_2O and CH_3OH to generate $Co(H)(CH_3OH)^+$. This intermediate, in a spin-allowed elimination involving the Co−H bond and a hydrogen atom from the methyl group of CH_3OH, then decomposes to a quartet state of $Co(CH_2OH)^+$ which is 6.0 kcal mol^{-1} higher in energy than ground-state $Co(OCH_3)^+$ having the same multiplicity. For the exclusive generation of $Ni(CH_2OH)^+$ two pathways were identified, both involving $Ni(X)(CH_3OH)^+$ (X = H, Br) as immediate precursors; in the subsequent evaporation of HX, the hydrogen atom originates from the methyl group of CH_3OH. DFT calculations (Figure 11) are not only consistent with the experimental observations but also explain why $Ni(CH_2OH)^+$ is formed rather than the thermochemically slightly more favorable $Ni(OCH_3)^+$ isomer. Here, the crucial point is that starting from ground-state triplet $Ni(H)(CH_3OH)^+$ (^{3}**6**), the spin-allowed reaction to produce $^3Ni(OCH_3)^+$ via ^{3}**TS6/7** cannot compete energetically with a reaction which, after spin inversion $^3\mathbf{6}\rightarrow{}^1\mathbf{6}$, proceeds via ^{1}**TS6/8** toward $^1Ni(CH_2OH)^+$.[92]

Finally, the celebrated $Ni(H)(OH)^+$ species[93] in the reaction with CD_3OH undergoes exclusive loss of HD, thus pointing to a clean activation of the methyl C−D bond.[85b]

5.2. Genuine Catalytic Cycles in the Gas-Phase Oxidation of Methanol

A conceptually rather attractive scheme for the Fe^+-catalyzed oxidation of methane that involves the conversion of CH_4 into CH_2O by O_2 in the presence of CH_3OH as a co-catalyst will be discussed first.[55,94] Oxygen-atom transport may proceed both in the formation of CH_2O from CH_3OH with O_2 as the O-atom

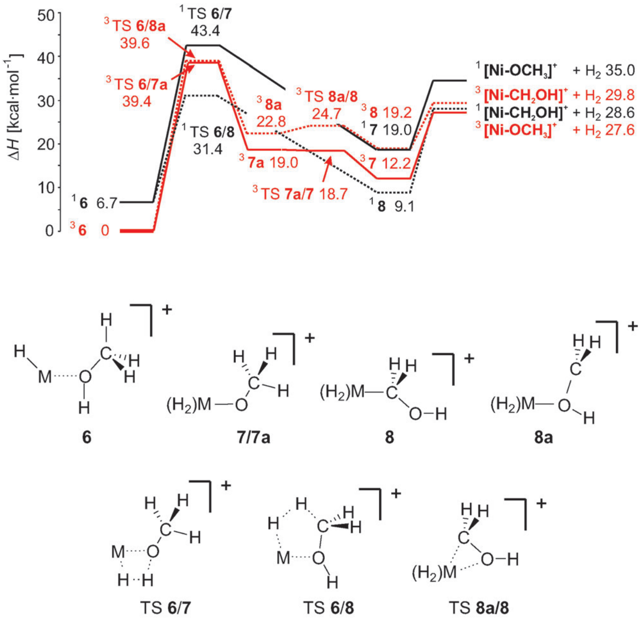

Figure 11. Potential-energy surface for the bond activation of methanol starting from triplet (red lines) and singlet (black lines) precursors $^{1,3}Ni(H)(CH_3OH)^+$ (^{1,3}**6**). The reaction paths involving O−H bond and C−H bond activations are shown in continuous and dashed lines, respectively. Both structures **7** and ^{3}**7a** correspond to $Ni(OCH_3)(H_2)^+$ complexes, with the H−H bond parallel and perpendicular to the NiOC plane, respectively; no bond activation is involved in ^{3}**TS7/7a**. ^{3}**TS8a/8** corresponds to a haptotropic metal shift from the oxygen atom to the carbon atom of the CH_2OH ligand. Relative energies are given in kcal mol^{-1} (adapted from Ref. [92]).

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donor for atomic Fe^+ and in the oxidation $CH_4 \rightarrow CH_3OH$ with FeO^+ [Eq. (11)–(13)].

$$CH_4 + \langle O \rangle \rightarrow CH_3OH \tag{11}$$

$$\underline{CH_3OH + O_2 \rightarrow CH_2O + H_2O + \langle O \rangle} \tag{12}$$

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \tag{13}$$

The key gas-phase experiments that mimic the overall Reaction (13) are summarized in Equations (14)–(17). The

$$\begin{aligned} &CH_4 + FeO^+ \rightarrow Fe^+ + CH_3OH \\ &\Delta_r H = -7\ \text{kcal mol}^{-1};\ k = 0.4 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \end{aligned} \tag{14}$$

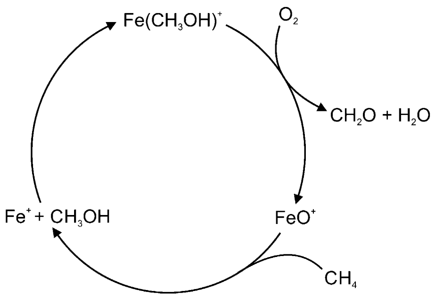
$$\begin{aligned} &Fe^+ + O_2 \rightarrow FeO^+ + O \\ &\Delta_r H = 39\ \text{kcal mol}^{-1};\ k \ll 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \end{aligned} \tag{15}$$

$$\begin{aligned} &Fe(CH_3OH)^+ + O_2 \rightarrow FeO^+ + CH_2O + H_2O \\ &\Delta_r H = -24\ \text{kcal mol}^{-1};\ k = 0.6 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \end{aligned} \tag{16}$$

$$\begin{aligned} &Fe^+ + CH_3OH \rightarrow Fe(CH_3OH)^+ \\ &\Delta_r H = -34\ \text{kcal mol}^{-1};\ k < 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \end{aligned} \tag{17}$$

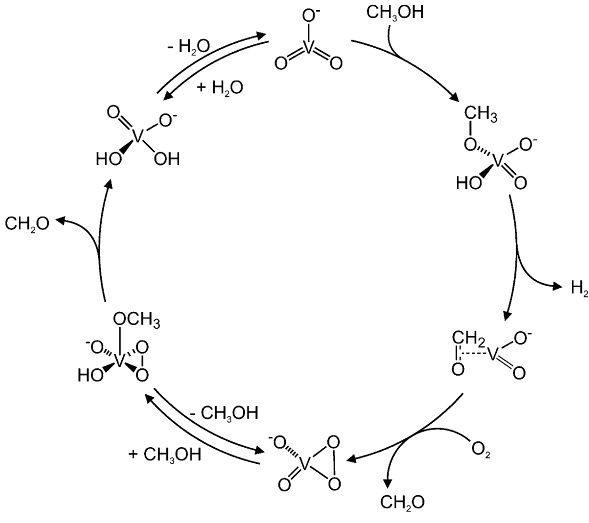
$\langle O \rangle$ equivalent of the reaction shown in Equation (11) is provided by FeO^+. Since FeO^+ cannot be generated directly from the Fe^+/O_2 couple on thermochemical grounds,[95] the decisive experiment is a methanol-mediated activation of dioxygen in which the alcohol serves as a co-reductant [Eq. (16)]. While this process is quite exothermic ($\Delta_r H = -24\ \text{kcal mol}^{-1}$), the rate efficiency is only about 10% as a result of spin barriers.[84,85,96]

A combination of the steps in Equations (14)–(17) leads to a viable sequence for the Fe^+-mediated oxidation of CH_4 to generate CH_2O according to Equation (13). Here, the CH_3OH molecule coordinated to the metal plays a central role both as a precursor for the oxidation product CH_2O and as a crucial intermediate in the activation of O_2. Furthermore, the co-formation of FeO^+ in Reaction (16) is quite remarkable in that over-oxidation (namely, the formation of Fe^+ and HCOOH) does not occur in this experiment, although bare FeO^+ rapidly reacts with formaldehyde.[97] The seemingly most simple step in Scheme 6, that is, the mere complexation of the iron cation by methanol [Eq. (17)], however, does not take place in the low-pressure regime (typically below 10^{-7} mbar). However, the magnitude of k_{17} can be enhanced with increasing pressure through ternary collisions.



Scheme 6. Catalytic sequence for the Fe^+-mediated oxidation of methane by molecular oxygen with methanol as a catalytic co-reductant. The side reaction of the FeO^+/CH_4 couple that leads to $FeOH^+/CH_3$ is omitted for clarity (adapted from Ref. [55]).

A completely different, rather interesting example has been reported by O'Hair and co-workers, who studied computationally and experimentally the reaction of VO_3^- with CH_3OH in the gas phase, including the re-oxidation of the catalyst.[98] The first step of the reaction corresponds to the addition of methanol so that the methoxy group coordinates directly to the vanadium atom and the hydrogen atom of the O–H group interacts with one of the oxygen atoms of VO_3^- (Scheme 7). In the second step, another hydrogen atom from the methyl group migrates to the newly formed hydroxy group, which leads to a complex of VO_2^-, water, and formaldehyde. This complex loses preferentially H_2O. Formaldehyde is subsequently replaced by molecular oxygen, and this step represents the reoxidation of V^{III} back to the V^V catalyst. The subsequent coordination of another methanol molecule proceeds in analogy with the first step, but the oxidation of the methoxy group to formaldehyde this time is not associated with the formation of a water molecule but with the reduction of the η^2-peroxy ligand. Elimination of the thus formed formaldehyde and subsequent water loss leads to the regeneration of the VO_3^- catalyst.



Scheme 7. Catalytic cycle for the gas-phase oxidation of two molecules of CH_3OH with O_2, mediated by VO_3^- (adapted from Ref. [98b]).

For the binuclear anionic dimolybdate clusters shown in Scheme 8, two gas-phase cycles have been identified, and in both cycles $Mo_2(O_6)(OCHR_2)^-$ (R = H, alkyl) acts as a central intermediate.[99] Three steps matter: 1) condensation of $[Mo_2O_6(OH)]^-$ with the alcohols R_2CHOH and elimination of water to produce an alkoxo-bound cluster; 2) oxidation of the alkoxo ligand and its liberation as an aldehyde or a ketone in a step which is rate-limiting and requires the supply of external energy through collisional activation; 3) regeneration of the catalyst by oxidation with nitromethane. The second cycle is similar, but differs in the order of the reaction

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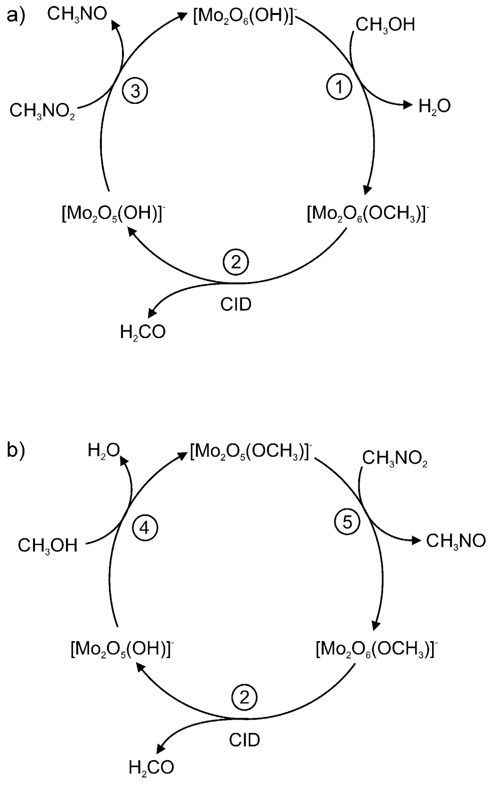

Scheme 8. a,b) Gas-phase catalytic cycles for the oxidation of methanol to formaldehyde. Reaction ② links $Mo_2O_6(OCH_3)^-$ and $Mo_2O_5(OH)^-$ and appears in both cycles, which differ in the sequence of the reactions with CH_3NO_2 and CH_3OH (adapted from Ref. [99]).

with the alcohol and the use of nitromethane as the terminal oxidant.

The role of the binuclear metal center was assessed by examination of the relative reactivities of the mononuclear $MO_3(OH)^-$ and binuclear $M_2O_6(OH)^-$ complexes (M = Cr, Mo, W). The molybdenum and tungsten binuclear centers (M = Mo, W) were reactive towards alcohols, but the chromium complex was not; this finding is consistent with the order of basicity of the hydroxo ligand in these anionic complexes. However, the tungsten complex $W_2O_6(OCHR_2)^-$ prefers a redox-neutral elimination of an alkene rather than oxidation of the alkoxo ligand to form an aldehyde or a ketone. This observation is in keeping with the oxidizing power of the anions. Interestingly, each of the mononuclear anions $MO_3(OH)^-$ (M = Cr, Mo, W) was inert to reaction with methanol, which highlights the importance of the second MO_3 unit in the catalytic cycles. Clearly, only the bimolybdate center has the appropriate balance of electronic properties that allows it to participate in each of the three steps; these gas-phase studies with well-defined cluster anions correspond to the unique role of molybdenum(VI) trioxide (MoO_3) in the industrial oxidation of methanol to formaldehyde at 300–400 °C.[100]

Finally, the dinuclear manganese oxide cations $Mn_2O_2^+$ and Mn_2O^+ were also found to act as catalysts in the gas-phase oxidation of CH_3OH.[101] As in the previous system, input of external energy (collisional activation or heating) is, however, essential for at least one of the reaction steps to close the catalytic cycle for the $Mn_2O_n^+$ ($n = 1, 2$) oxides.

5.3. Comparison of a Model System with a Real Catalyst

While most of the gas-phase experiments rely on charged systems and therefore are somewhat limited in scope, in an in silico experiment, that is, computations, the intermediates and transition states assumed to be involved in a catalytic cycle do not suffer from this limitation; in addition, the structural complexity of the species can be modified at will and adjusted to both the gas-phase models and the real catalyst. Here, we will describe some aspects of the $CH_3OH \rightarrow CH_2O$ conversion for which silica-supported vanadium oxides serve as real catalysts. This reaction has also been studied in the gas phase in quite some detail using $VO(OCH_3)_3^+$ and larger vanadium oxide clusters as models,[83r,88,102] and extensive computational work also exists.[77h,103] The computed reaction sequence commences with adsorption of the substrate on the surface, the latter having a presumed vanadyl-site structure VO(O–Si–)$_3$ (Figure 12). This step is associated with the cleavage of one of the V–O–Si bridges and provides $VO(OCH_3)$(O–Si–)$_2$ and HOSi– sites. Next, a hydrogen atom from the methoxy group is transferred to the terminal vanadyl oxygen atom, which results in the formation of formaldehyde. The model compound $VO(OCH_3)_3$ thus mimics an intermediate in which two methoxy groups represent the missing O–Si links to the silica support, while the remaining part is realistic. In the

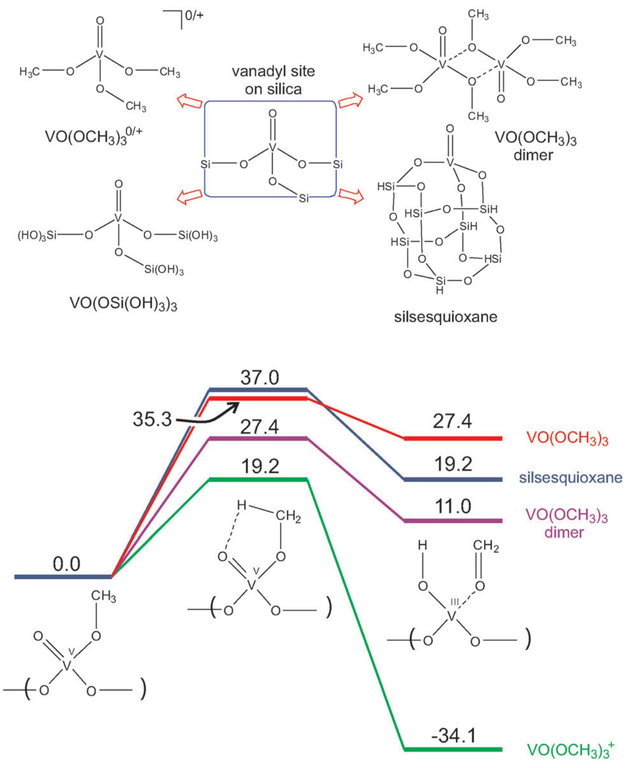

Figure 12. Different models for a vanadyl site of a silica-supported vanadium oxide catalyst for the $CH_3OH \rightarrow CH_2O$ conversion, as calculated using B3LYP/TZVP; relative energies are given in kcal mol^{-1} (adapted from Refs. [4n,103b]).

singly charged state, the model corresponds to the V^{V} oxidation state with a radical site located at the oxygen atom of the V=O unit; rearrangement leads to the V^{IV} radical species coordinated to formaldehyde (Figure 12). The overall reaction within this distonic radical cation is exothermic. The energy barrier predicted at the B3LYP level (ca. 19 kcal mol^{-1}) is slightly overestimated, as revealed by a comparison with the threshold photoionization study of the dissociation of $VO(OCH_3)_3^+$; the latter suggests a barrier of about (13 ± 2) kcal mol^{-1}. The same model reaction in the *neutral* state shows similar results as far as the geometry and the formal oxidation states of the vanadium sites of intermediates and products are concerned; however, the corresponding reaction step is *endothermic*, as are experiments with real catalysts. Thus, in this case, while the charged model provides hints as to the reaction mechanism and suggests possible structures of intermediates, it cannot be taken as a reliable guide for energetic considerations.[103a]

As a further test for the relevance of such simplified models, a comparison of $VO(OCH_3)_3$ with larger model compounds, such as the dimer of $VO(OCH_3)_3$, $VO[OSi(OH)_3]_3$, or vanadyl silsesquioxane (Figure 12) has been made. The dimer of $VO(OCH_3)_3$ exhibits a reactivity that is qualitatively analogous with that of the monomer. The next two models, $VO[OSi(OH)_3]_3$ and silsesquioxane, offer the possibility to study the first reaction step, that is, the adsorption of methanol on the catalyst. This step leads, in the case of the $VO[OSi(OH)_3]_3$, to free $Si(OH)_4$, which is stabilized by the formation of intramolecular hydrogen bonds.[104] As this option is not available in a real catalyst, this model overestimates the adsorption energy (21 kcal mol^{-1}). In the case of the vanadyl silsesquioxane complex, the addition of methanol to the model catalyst is accompanied by the formation of an integrated −O−Si(H)(OH)−O− unit, and therefore, the results can be expected to be more accurate. Accordingly, the adsorption energy drops substantially to 9.6 kcal mol^{-1}. Next, hydrogen rearrangement within the $-O-VO(OCH_3)-O-$ unit occurs, and the activation energy for this step is calculated to be around 48 kcal mol^{-1} for the $VO[OSi(OH)_3]_3$ model and 48.5 kcal mol^{-1} for silsesquioxane. Final optimization using the broken-symmetry approach, correction for the spin contamination, and the inclusion of zero-point vibrational energy lowers the energy barrier to 37 kcal mol^{-1} (Figure 12). This value is in rather good agreement with the experiments conducted with real systems; therefore, the model approach appears adequate.[103a,104]

Other examples for using gas-phase experiments with "isolated" reagents as models for mimicking reactions in the condensed phase include 1) the Degussa process, that is, the platinum-mediated coupling of methane and ammonia to generate HCN,[5] 2) the mechanistic understanding of the Cytochrome P450 mediated C−H bond oxygenation[62,63] based on a detailed analysis of the most simple system, that is, FeO^+/H_2,[63,96] or 3) the relationship between the rich gas-phase chemistry of bare PtO_2^+[105] and the extraordinary features exhibited by high-valent platinum oxides,[106] just to mention a few.

6. Conclusions

> "*It remains a source of frustration to know so much about the reactions of transition-metal ions with hydrocarbons and yet have so many questions remain unanswered.*"
>
> Peter B. Armentrout, Jack L. Beauchamp, 1989[107]

On this rather depressing note, Armentrout and Beauchamp concluded their superb review on the fundamental aspects of gas-phase organometallic chemistry. Considering the difficulties encountered at that time in elucidating mechanistic aspects of reactions occurring at a *single* metal center, it was not surprising that processes of higher complexity involving clusters, surface reactions, and metal catalysts were considered as "*largely shrouded in mystery*".[107] However, things have changed since the landmark paper of Allison, Freas, and Ridge in 1979[108a] about the first example of gas-phase activation of alkanes by "naked" transition-metal ions, the seminal Kappes–Staley report[108b] on genuine, homogeneous gas-phase catalysis by bare Fe^+, and the Armentrout–Beauchamp review in 1989[107]—and, fortunately, things have changed for the better! This is in no small part due to the breath-taking instrumental improvements (laser desorption, electrospray ionization, Smalley-type cluster-ion sources, multipole analyzer, ion traps, gas-phase ion spectroscopy, ion-mobility experiments, or ion-electron diffraction, to name but a few) which permit experiments which were thought of as simply impossible two decades ago. Structures of gaseous, medium-sized species of any charge state can now be routinely identified spectroscopically and thus form a reliable starting point for reactivity studies.[109] Conceptually, the development of new mechanistic paradigms, such as two-state reactivity[17] or appreciating the role of relativistic effects[12–14] in bond-activation processes, has removed some of the mysteries and are now considered relevant in several areas far beyond the field of gas-phase organometallic chemistry.[62,64] Further, the inclusion of ligated systems[4j,m,n,110] not only extends beyond the world of "idealized" naked-atom chemistry; these systems also serve as more realistic models for reactive species or intermediates that are capable of activating methane in the condensed phase, as do the exciting cluster studies aimed at mimicking surface reactions.[4a,g,k,l,n,22,24,48b,c,83,111] A major breakthrough certainly was driven by computational chemistry. While open-shell, electronically and coordinatively unsaturated transition-metal systems still pose non-trivial problems,[112] the progress made in the last two decades is nearly unparalleled—and that applies not only to gas-phase studies[113] but extends also to the most complex surface reactions.[31a,114] Actually, the quality of contemporary computational studies is such that theoretical work no longer only complements or explains experimental findings *after* the fact; rather, theory occasionally challenges experimentalists by predicting the fleeting existence of particularly reactive species which have not yet been generated.[115]

There is indeed good reason to argue that an integrated approach, as intended and already realized to some extent by UniCat,[116] will also help to cope with the persisting challenges associated with the activation of small molecules,

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for example, methane or carbon dioxide.[117] Thus, at long last, bridging the gap between chemistry conducted at an atomic level in the gas phase and the most complex behavior at surfaces[118] or in solution[119] seems possible, provided scientists do not ignore Gerhard Ertl's gentle reminder about the relationship between the simple and the complex, as depicted in Figure 13.[120]

Figure 13. From the simple to the complex (with courtesy from G. Ertl, Berlin, Ref. [120]). The text reads, "A baguette is more than the sum of its crumbs."

7. Addendum

Since the submission of this review article, numerous publications have appeared which have a bearing on the topics discussed here. Among these studies, together with a few articles which were not included originally, the following ones deserve brief mentioning.

An exhaustive review on the role of organometallic intermediates on the active centers in surface-mediated C–H bond activation has been published by Coperét,[121] and the state-of-the-art of theoretical descriptions of surface reactions, aimed at engineering the electronic structure of the active surface sites, forms the focus of a review by Norskøv et al.[122]

With regard to the dehydrogenation of methane (Scheme 1, process ①) by singly or doubly charged actinide ions (An^+ or An^{2+}), the role of 5f electrons and orbitals has been analyzed both computationally and experimentally.[123] Of particular importance is the finalizing that the insertion efficiency to produce $C{-}An^{2+}{-}H$ or $C{-}An^{+}{-}H$ species is related to the energy needed to promote the An^+/An^{2+} ions from their ground state to a prepared divalent state with two non-5f-valence electrons.[124] In addition, in the exothermic reaction of, for example, Th^{2+} with CH_4, a spin crossing from the ground-state triplet reactant to the excited singlet surface of the products is necessary to bring about thermal dehydrogenation. Possible origins of the anomalously low reactivity of Pt_4^+ towards CH_4[22,23d] has been discussed at great length using DFT-based calculations.[125]

In the context of homolytic C–H bond cleavage [Eq. (8)], quite a few studies have been performed recently. In addition to the hydrogen-atom abstraction from CH_4 by $PbO^{+\bullet}$,[42] the congeners $GeO^{+\bullet}$ and $SnO^{+\bullet}$ exhibit parallel behavior both in terms of efficiencies and kinetic isotope effects.[126] Extremely insightful experimental and computational studies on this topic were conducted by He, Ding, and co-workers.[127] This work once more underlines the crucial role that oxygen-centered radicals play in the hydrogen-atom transfer (HAT), irrespective of the charge state; in fact, the calculated spin density at the terminal oxygen atoms in cluster oxides could be correlated with the observed rate constants, and evidence was presented how, by a proper choice of the chemical composition of the cluster oxides, a fine tuning of the spin density can be achieved.[127b] These findings, together with those described in Section 3, are of quite some importance in the conceptual understanding of HAT in solution. Here it has been suggested[128] that "*the presence of unpaired spin density at the abstracting atom is not a requirement for, or a predicator of, HAT reactivity*",[128a] and that HAT is better described by a coupled electron/proton transfer, that is, $H^{\bullet} \cong e^- + H^+$. In the latter, the electron is transferred to the highly electrophilic metal (often in a high oxidation state), and the proton to the basic (oxygen) ligand. As far as gas-phase reactions are concerned, without any exception, thermal HAT requires the presence of unpaired spin density at the abstracting oxygen atom. This view is also supported by the recently described $CuO^{+\bullet}/CH_4$ couple.[129] Here, the ground-state triplet of $CuO^{+\bullet}$ with a spin density of 1.68 at the oxygen atom brings about, at room temperature, HAT with an efficiency of 20 % and an intramolecular KIE of 2.6. The competing $CH_4 \rightarrow CH_3OH$ conversion, having an efficiency of 31 %, occurs after a triplet–singlet switch, that is, the $CuO^{+\bullet}/CH_4$ system demonstrates spin-selective reactions in the thermal activation of methane.

For the $CH_4 \rightarrow CH_3OH$ conversion, several new articles addressing different aspects of this problem have also surfaced recently. Gunnoe and co-workers describe in a minireview strategies and fundamental advancements,[130] the identification of reactive intermediates by matrix-isolation infrared spectroscopy has been reviewed by Wang and Zhou,[131] theoretical aspects of the cytochrome P450 mediated methane oxidation form the subject of articles by Hu et al.[132a] and the Shaik group,[132b] tuning a P450 enzyme by protein engineering has been reported by Reetz and co-workers,[133] and, finally, the role of Fe-doped zeolites[68] in the oxidation of CH_4 by N_2O was reported as early as 1998.[134]

For the mechanism of the $CH_3OH \rightarrow CH_2O$ oxidation (Section 5), the work of Mavrikakis and co-workers[135] is worth mentioning; the authors present a microkinetic model together with detailed experimental studies on the platinum-mediated decomposition of CH_3OH and demonstrate that the reaction commences with scission of the C–H bond, according to Scheme 4, path Ⓑ; this step is also rate-limiting. For iron–vanadate catalysts, often employed for this reaction, in recent studies the nature of the catalytically active site has been identified, and it was shown that O–H bond activation (Scheme 4, path Ⓐ) initiates the methanol oxidation.[136,137]

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