Selective Activation of Alkanes by Gas-Phase Metal Ions[†]

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1. Introduction

The importance of the selective activation of alkanes for science and technology in the forthcoming decades does not need to be explicitly pointed out in this thematic issue of *Chemical Reviews*. Instead, we would like to summarize the development and the state-of-art of experimental and theoretical methods for the investigation of model reactions for alkane activation in the gas phase.[1] However, before doing so let us address the question, how other scientists, both in academia as well as industry, can profit from such model studies in the gas phase, usually involving very small, charged species under conditions in a mass spectrometer which are very far from real catalysis. To this end, we refer to the synthesis of HCN as a reasonably simple example of how large-scale technical processes can be investigated in microscopic models.

Jana Roithová (right), Ph.D., leads a group on the topic of reaction mechanisms at the Faculty of Science at the Charles University in Prague. Her research is based on the synergy of gas-phase experiments and theoretical calculations. She received her Ph.D. degree in the group of Prof. Zdenek Herman (J. Heyrovsky Institute of Physical Chemistry, Prague) on the topic of reactivity of small molecular dications in 2003. Since then she has made key contributions to superelectrophilic chemistry in the gas phase, with particular attention toward the activation of nonreactive substrates such as rare gases, nitrogen, and methane. Recently, she concentrates her research on the properties of redox-active molecules, their interactions with transition metals, and mechanisms of organometallic reactions. She is author of more than 80 papers and received, among others, a "L'Oréal for Women in Science" stipend and the Hlavka prize.

Detlef Schröder (left), Dr. habil., is group leader for spectroscopy and physical-organic chemistry at the Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences in Prague. He studied chemistry at the TU Berlin (Berlin, Germany), where he also did his Ph.D. with Prof. Helmut Schwarz in 1992 on selective bond activations by transition-metal ions, for which he received the Schering-Award. Dr. Schröder is author of more than 350 scientific papers which cover various areas of gas-phase ion chemistry, ranging from properties of diatomic molecules via organic reaction mechanisms and studies in oxidation catalysis to gas-phase models of enzymatic processes. Among others, his current interests concern selective bond activation, multiply charged systems, and combination of different spectroscopic techniques for the on-line monitoring of chemical reactions.

[†] In memoriam of Dr. Andreas Fiedler.

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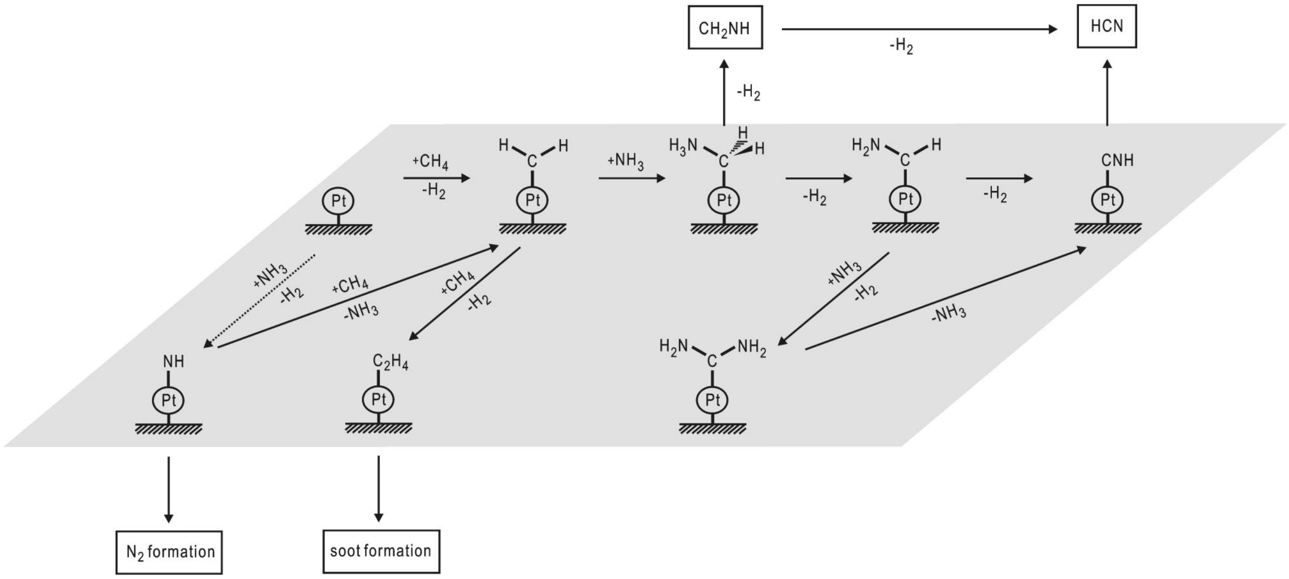


Figure 1. Conceptual model of the Degussa process derived from gas-phase studies of the reactions of bare platinum cation with methane and ammonia (adopted from ref 3c).

The Degussa process for the large-scale synthesis of hydrogen cyanide from methane and ammonia in platinum coated hot tubes (reaction 1)[2] was first modeled by an investigation of a single, bare platinum cation, Pt^+, reacting with methane and ammonia, respectively.[3] Obviously, this is an extreme simplification which appears very remote from applied catalysis.

$$CH_4 + NH_3 - Pt \rightarrow HCN + 3H_2 \qquad (1)$$

The first, honest answer to the above question about the value for other scientists is thus that no gas-phase model system can ever predict the rate constants relevant for a catalytic process or even more complex parameters such as turnover numbers and turnover frequencies. In fact, none of the gas-phase results can be transferred to the bulk in a 1:1 fashion.[4]

The second, more complex answer is that gas-phase studies can nowadays often permit rather useful insights into the elementary steps of catalytic processes and thereby contribute to catalyst research in a valuable manner. In the context of the Degussa process, for example, a straightforward investigation of the atomic Pt^+ cation could provide an explanation for the particular selectivity of platinum catalysts in reaction 1. Thus, the bare Pt^+ cation efficiently reacts with methane (reaction 2),[5] while it does not activate ammonia.[3] In contrast, the $PtCH_2^+$ cation formed in the first step preferentially reacts with ammonia, rather than methane, leading to C−N coupled products (reactions 3a and 3b).

$$Pt^+ + CH_4 \rightarrow PtCH_2^+ + H_2 \qquad (2)$$

$$PtCH_2^+ + NH_3 \rightarrow PtCH(NH_2)^+ + H_2 \qquad (3a)$$

$$PtCH_2^+ + NH_3 \rightarrow PtH + CH_2NH_2^+ \qquad (3b)$$

Moreover, mechanistic considerations concerning the products being formed imply that after the C−N coupling step there exist two independent routes for the formation of HCN: a surface-bound pathway via metal-aminocarbenes and a gas-phase route involving formimine.[3,6] In conjunction with labeling experiments, kinetic studies, and theoretical work, the analysis of the reactions of atomic Pt^+ with methane and ammonia thus led to a first-principle proposal for the elementary pathways in the Degussa process (Figure 1).

Subsequent systematic studies of several late transition-metal ions led to the educated speculation—no more than that at this time—that combinations of more than one transition metal might increase selectivity for HCN production.[3c] On this occasion, the so far by and large informal contact with industrial partners became much more intense and led to a considerable donation for the construction of a cluster-ion source on the one hand and a patent about bimetallic catalysis on the other.[7] With the cluster source,[8] the earlier speculation based on atomic ions that the combination of gold and platinum may be beneficial[3c] could be verified in that from the diatomic clusters Pt_2^+, $PtAu^+$, and Au_2^+ only the mixed cluster $PtAu^+$ can mediate both steps involved in the C−N coupling of methane and ammonia.[9−11] This short example for the interplay between basic research and industrial practice may thus serve to illustrate that the seemingly esoteric gas-phase studies may well have an impact on applied catalysis.

However, there is yet a third answer to the above question, and this is related to the usage of the more and more powerful theoretical methods in the modeling of catalytic processes. Thus, for small systems, there nowadays exist computational codes which brought the theoretical predictions to a precision and accuracy which are even superior to experiment in many respects. Nevertheless, computations including just a single transition-metal atom are already not to be considered as trivial. Highest level calculations of compounds with heavy elements require explicit inclusion of the rather important relativistic effects and are still today limited to species consisting of only few atoms, e.g. $PtCH_2^+$.[8] For the investigations of larger systems, reasonable compromises in the theoretical treatment (both methods and basis sets) need to be made. In this respect, a key requirement is the evaluation of the theoretical tools by some accurate benchmark experiments. While *structural parameters* such as bond distances or vibrational frequencies of the reactants, intermediates, and products might be available from surface studies, gas-phase experiments can provide accurate *energetic data* for benchmarking theoretical work. In the above case of methane activation by bare Pt^+, for example, it could be shown that reaction 1 and its reversal 1′ are in thermal equilibrium.[5d,g]

$$PtCH_2^+ + H_2 \rightarrow Pt^+ + CH_4 \qquad (1')$$

Detailed analysis of the equilibrium data as well as complementary measurements of absolute reaction thresholds provided $D(Pt^+{-}CH_2) = (4.80 \pm 0.03)$ eV as an accurate benchmark for theory.[5g] Thus, gas-phase experiments serve as a direct link to theory and careful evaluation of the performance of the latter by benchmarking allows accurate assessment of the quality of theoretical predictions for larger systems. In brief, gas-phase studies cannot "predict" applied catalysis but may well provide useful, even "valuable" inspiration and in any case serve as reference points for modern theoretical approaches.

In the following, we begin with some considerations about selectivity in chemical processes and elementary reactions; then we very briefly present the most important experimental methods, followed by a description of the gas-phase activation of alkanes by (i) bare transition-metal atoms in various charge states, (ii) simple ligated metal species such as metal carbonyls, metal halides, or metal oxides, and (iii) larger complexes and analogs for homogeneous catalysts generated directly from solution. With respect to the substrates, we by and large restrict ourselves to alkanes; specifically, reactions of substrates with activated C−H bonds (e.g., allylic, benzylic, or enolic positions) as well C−H bond activations which follow after an insertion step into a C−X bond (X = heteroatom) are excluded. The section about the experimental efforts is followed by a description of the various theoretical approaches in the field. However, we mostly restrict ourselves to cases in which specific information about the selectivity of C−H bond activation is available from either experiment or theory, which are briefly outlined in a separate section, also including the directed C−X bond activations (X = H, C, Si) in metal−cation complexes of monofunctionalized alkanes. Likewise, we restrict the description of the very rich and highly interdisciplinary field of transition-metal clusters to the few studies which provide direct insight about the selectivity in the bond activation processes observed. In fact, in most experimental studies of cluster reactions the nature of intermediates and products is rather vaguely defined because the experimental tools developed for the structure elucidation of mononuclear transition-metal compounds first have to be adapted to oligonuclear species and also the theoretical methods for the transition-metal clusters with several unpaired d electrons per atom first have to be developed further.

2. Definition of Selectivity in Gas-Phase Ion Chemistry

Before coming to the experimental and theoretical studies, two general aspects in the interplay of gas-phase ion chemistry and applied sciences will be addressed, because the concepts in applied synthesis or catalysis cannot be translated to gas-phase experiments in a 1:1 scheme, or vice versa.[4,12] This should by no means imply that both regimes do not have anything in common. However, in the extrapolation from high to low pressures, the particular conditions of both regimes have to be acknowledged.

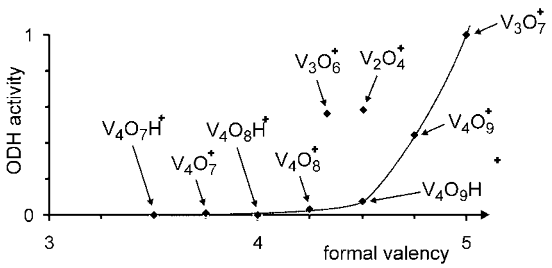


Figure 2. Relative ODH activity of $V_mO_n^+$ cluster ions as a function of the average formal valence of vanadium.

2.1. Measures for Reactivity

In the condensed phase, the performance of a catalyst is inter alia characterized by the turnover frequency (TOF = number of reactions one catalyst molecule mediates per second) and the turnover number (TON = number of reactions one catalyst molecule mediates during its entire lifetime). While a few examples of real catalytic cycles have been realized in the gas phase,[13,14] TOF and TON are not suitable concepts for gas-phase reactivity studies of C−H bond activation for two reasons. (i) On the one hand, many reactions of highly reactive gas-phase metal species are diffusion-limited, which means that the reactions occur with the gas-kinetic collision rate (k_c) and hence the maximally possible rate constant. If another species would even be more reactive in a general sense, in the gas-phase measurement the mere kinetic outcome would be the same. (ii) On the other hand, many transition-metal ions do not react at all with more inert substrates (e.g., methane or alkanes in general), but they do activate C−H bonds in a broad variety of functionalized substrates. Thus, the experimental rate constants for several substrates are zero, even though other substrates undergo activation, such that the consideration of the rate constant for a single substrate is not an appropriate measure for the ability of a certain species to activate C−H bonds in terms of a TOF. Likewise, the TON is only accessible for systems in which a complete catalytic cycle can be realized in the gas phase. In the few cases in which this has been possible,[13] the TONs were frequently limited by background impurities in the vacuum systems and TON values attractive for applications in heterogeneous catalysis ($>10^6$) simply cannot reliably be sampled in high-vacuum devices.

As an alternative measure for the ability of various metal ions to activate a certain type of chemical bonds or to mediate a certain chemical process, the relative reactivity of a set of metal ions $[M]_1 - [M]_i$ for a set of neutral reactants $R_1 - R_j$ ion partners has been introduced (eq 4).[15]

$$k_{rel}([M]_i) = \sum_j k([M]_i,R_j) / \sum (\max)_{i,j} k([M]_i,R_j) \qquad (4)$$

Thus, a series of substrates rather than a single compound is considered, and the most reactive ion serves as a reference for the relative reactivities of the others. As an example, we refer to the activity of $V_mO_n^+$ cluster ions for the oxidative dehydrogenation (ODH) of hydrocarbons,[16] where 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutene were used as model compounds. Quite obviously, there exists a correlation between the ODH activity and the formal valence of the vanadium atoms in the $V_mO_n^+$ clusters, with a maximum for the high-valent vanadium species, as expected (Figure 2).[17]

Conceptually, the consideration of more than one neutral reaction partner fulfills a 2-fold screening effect in that (i) possible control of the overall reaction by the lifetimes of the initial encounter complexes as well as (ii) possibly differentiated barriers for the various ionic and neutral reagents are smoothed by the consideration of different substrates. Moreover, the averaging of several experimental data sets in the relative reactivities lowers the effects of accidental experimental errors. With respect to the choice of the set of reactants, a well-tempered selection is to be achieved. Specifically, the set should include substrates which are more difficult to activate (e.g., alkanes in the order methane < ethane < propane < *n*-butane < isobutane, etc.) via compounds with activated C−H bonds (e.g., olefins in the order propene < isobutene <1- and 2-butene) to compounds which are activated rather easily (e.g., 1,4-cyclohexadiene). A less reactive species will only react with the last members of the set, whereas the most reactive representatives will react with all of them, although in possibly accentuated rates.

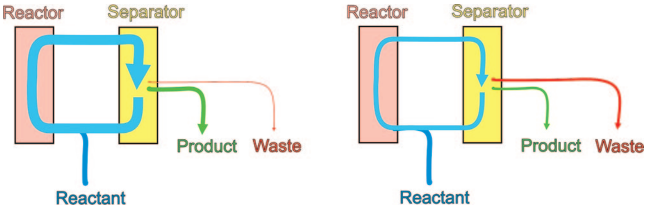
2.2. Definition of Selectivity in Ion Reactions

The selectivity (S) of a chemical process for a desired product P_1 is defined as $S(P_1) = x(P_1)/\sum_i x_i(P_i)$, where $x_i(P_i)$ stands for the molar fraction x_i of the products $P_1 - P_i$. A frequent mistake is that selectivity is considered identical to the chemical yield of the desired product, which is not at all correct in many processes in industrial chemistry, particularly in alkane activation. Thus, the second important parameter is the conversion of the reactant R, which is defined as $X(R) = \sum_i x_i(P_i)/[x(R) + \sum_i x_i(P_i)]$. In an ideal case, conversion as well as selectivity would be 100%. In the activation of alkanes, however, selectivity and conversion quite often oppose each other. Let us consider the oxidative dehydrogenation of propane (ODP)[18] according to reaction 5 as an example.

$$C_3H_8 + {}^1/_2O_2 - \text{cat.} \rightarrow C_3H_6 + H_2O \qquad (5)$$

At low conversions (typically a few percent), the selectivity for propene formation can be up to 100%. A higher conversion of propane means, however, that not only the reactant but also already the product has a significant residence time on the catalyst, which very much deteriorates selectivity for two simultaneously operating reasons. At first, propene formed as the product of ODP is a potentially much better ligand for any coordinatively unsaturated metal center than the saturated hydrocarbon propane serving as the reactant. Second, propene has allylic C−H bonds which are much more prone to undergo bond activation than the C−H bonds in the saturated hydrocarbon propane. Both effects combine in that the residence time of propene at the active sites of the catalyst is longer than that for propane, while oxidation is more likely to occur for the olefin in comparison to the alkane. As a result, the selectivity for ODP often drops rapidly with increasing conversion. From an economic point of view, this requires a compromise between high selectivity at low conversion and thus high cycling loads as well as reactor volumes on the one hand and lower selectivity at larger conversion and reduced cycling loads as well as reactor size (Scheme 1). The dilemma between selectivity and conversion in the partial oxidation of alkanes accordingly also highlights the importance of basic research in this area.

Scheme 1. Sketch of the Conversion/Selectivity Dilemma in Partial Oxidation Reactions[a]



[a] At low conversion (left), the desired product is formed with a high selectivity, but the cycling load is high. At large conversion (right), overoxidation of the primary products leads to increased amounts of byproducts (here designated as waste).

In ideal gas-phase experiments, the so-called single-collision conditions are maintained strictly in order to ensure that only the bimolecular reaction of interest is studied. As a direct consequence, the above definition for selectivity of a given chemical process *a priori* cannot be applied, because the single-collision conditions by themselves forbid consecutive reactions of the primary reaction products. Accordingly, many elementary reactions formally bear selectivities of 100%, although comparative studies with more complex substrates, conditions, or processes demonstrate that the actual selectivities are rather poor. One approach toward more realistic considerations are systematic investigations of not only the first but all conceptually conceivable subsequent steps. In the case of ODP (reaction 5), for example, this would include consideration of not only the initial oxidation of propane by the model species but also the reaction of the same model species with the primary products such as propanol and propene. Such an option is conceivable in gas-phase experiments and also has been realized in a few cases,[19,20] but it is of limited generality due to three general reasons.

(i) A comparison of absolute rather than relative rate constants needs to be made which is associated with substantially increased experimental uncertainties.

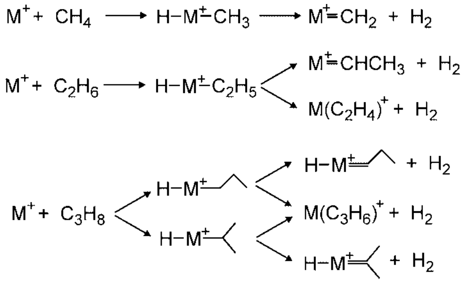
(ii) For those metal species which can activate alkanes, many gas-phase reactions with the primary products of oxidation (olefins, alcohols, etc.) occur at the collision rate. In other words, they are diffusion-limited rather than determined by the relevant activation barrier(s); under real conditions, the ratio of the secondary to the primary oxidation reactions might thus still be much larger.

(iii) In addition to the mere rate constants of the elementary steps, the residence time of the various intermediates at the active sites is of vital importance for the assessment of the rate laws in catalysis. Ligand-binding energies determined in gas-phase experiments can provide very useful hints in this respect, but the conversion of binding energies to idealized model systems into residence times at the (highly divergent) active sites of a catalyst is all but trivial.

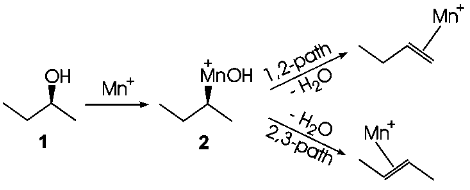
In order to appropriately adapt to the gas-phase experiments, we will therefore define the term selectivity with respect to a single molecule in which different reaction pathways are possible. For methane and ethane, for example, only a single option exists for C−H bond activation by a bare metal cation, but already in the next step, e.g. a dehydrogenation, two different routes are conceivable for ethane. In the case of propane, the pathways split already in the initial step, i.e. activation of primary versus secondary C−H bonds, and the divergence in the dehydrogenation channel is even larger (Scheme 2).

In contrast to the selectivity of chemical processes in applied processes, we accordingly relate the term selectivity

Scheme 2. Divergence of Different Pathways for C−H Bond Activation with Increasing Size of the Hydrocarbons



Scheme 3. Mechanism of the Mn$^+$-Mediated Dehydration of 2-Butanol To Afford either (1-butene)Mn$^+$ or (2-butene)Mn$^+$



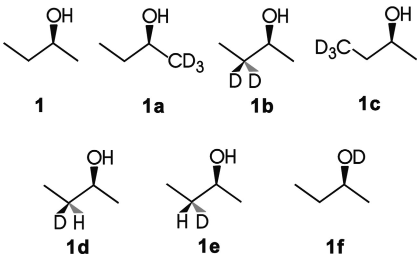
to a specific type of reaction of a given substrate (e.g., 1,1- versus 1,2-dehydrogenation of ethane) or even a certain elementary step (e.g., activation of primary versus secondary C−H bonds). We note in passing the similar uses of the term selectivity in organic synthesis, where orientation often matters much more than the overall yield, when it comes to aspects of regioselectivity, as for example in the electrophilic substitution of arenes, the endo/exo selectivity in Diels−Alder reactions, or diastereo- and enantioselectivity in asymmetric synthesis.

Before closing this section, we provide one example for the way in which selectivities are evaluated in mass spectrometric experiments, where the amount of ions is much too small to allow for any conventional kind of preparative isolation and subsequent spectroscopic analysis of the products being formed.[21] For the evaluation of the selectivity of a certain process, regiospecific isotope labeling is most insightful. As a simple example for illustration of this technique, we refer to the dehydration of 2-butanol by Mn$^+$, which involves insertion of the metal into the C−OH bond (**1** → **2**, Scheme 3) followed by β-H transfer and liberation of water. The task is thus to determine (i) the selectivity of the dehydration, including the consideration of possible H/D exchange processes and (ii) the regioselectivity of the β-H transfer, which can lead to either a terminal or internal olefin (1,2- versus 2,3-pathways in Scheme 3).

For answering this task and moreover also addressing the diastereoselectivity of C−H bond activation, Mn$^+$ complexes of the specifically deuterium labeled compounds **1a**−**1f** (Chart 1) are discussed as an example.

Table 1 shows the distribution of H_2O and HDO losses observed for the various complexes. Prior to a more detailed analysis using kinetic modeling (see below), it is pointed out that the exclusive loss of HDO from **1f**/Mn$^+$ indicates that the hydroxy group stays intact throughout the reaction and does not participate in H/D exchange reactions. Thus, the only task remaining is the origin of the second hydrogen atom. Interestingly enough, however, this C−H bond activation involves a notable stereospecific effect (SE) because the ratios of H_2O and HDO losses from the diastereomeric complexes **1d**/Mn$^+$ and **1e**/Mn$^+$ differ significantly.

Chart 1. Deuterium Labeled 2-Butanols 1a−1f[a]



[a] Note that all compounds were synthesized in racemic form, while **1d** and **1e** are diastereoselectively labeled.

Table 1. Normalized Intensities[a] of H_2O and HDO Eliminations in the Mn$^+$-Mediated Dehydration of 2-Butanol[b]

substrate		H_2O	HDO
$CH_3CH(OH)CH_2CH_3$	**1**	100	
$CD_3CH(OH)CH_2CH_3$	**1a**	85	15
$CH_3CH(OH)CD_2CH_3$	**1b**	32	68
$CH_3CH(OH)CH_2CD_3$	**1c**	98	2
syn-$CH_3CH(OH)CHDCH_3$	**1d**	67	33
anti-$CH_3CH(OH)CHDCH_3$	**1e**	75	25
$CH_3CH(OD)CH_2CH_3$	**1f**	<2	>98

[a] $\Sigma = 100\%$. [b] The measurements were done by sampling the metastable ions of mass-selected 2-butanol/Mn$^+$ complexes generated by chemical ionization.

Qualitatively, the data in Table 1 indicate a clear preference for the 2,3-pathway in Scheme 3, as revealed by the observation that the amount of HDO lost from **1b**/Mn$^+$ is much larger for **1a**/Mn$^+$. Further, the participation of the C(4) position is small (see data for **1c**/Mn$^+$). Without explicit acknowledgment of kinetic isotope effects, these considerations remain qualitatively, however, because the labeling itself can crucially influence the branching. Provided that the set of labeled compounds is sufficiently large and diverge enough, the experimental patterns can be used to determine the crucial parameters involved by means of kinetic modeling. To this end, we express the regioselectivities for the transfer of the final hydrogen atom from the positions C(1)−C(4) in 2-butanol as the relative rate constants k_1−k_4 with $\sum k_i = 1$, include the stereospecific effect (SE) for the diastereospecifically labeled compounds **1d** and **1e**, and apply a common kinetic isotope effect (KIE) associated with hydrogen transfer. In this way, the H_2O/HDO ratios from the complexes **1a**/Mn$^+$−**1e**/Mn$^+$ can be described by eqs 6a−6e.

$$\mathbf{1a}/\mathrm{Mn}^+:\quad I_{\mathrm{H_2O}}/I_{\mathrm{HDO}} = (k_2 + k_3 + k_4)/(k_1/\mathrm{KIE}) \tag{6a}$$

$$\mathbf{1b}/\mathrm{Mn}^+:\quad I_{\mathrm{H_2O}}/I_{\mathrm{HDO}} = (k_1 + k_2 + k_4)/(k_3/\mathrm{KIE}) \tag{6b}$$

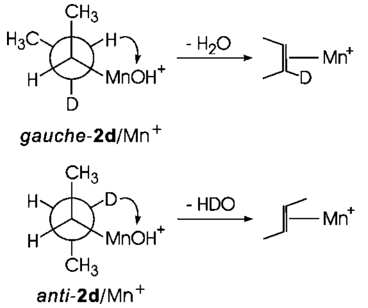
$$\mathbf{1c}/\mathrm{Mn}^+:\quad I_{\mathrm{H_2O}}/I_{\mathrm{HDO}} = (k_1 + k_2 + k_3)/(k_4/\mathrm{KIE}) \tag{6c}$$

$$\mathbf{1d}/\mathrm{Mn}^+/\quad I_{\mathrm{H_2O}}:I_{\mathrm{HDO}} = (k_1 + k_2 + {}^1/_2k_3/\mathrm{SE} + k_4)/({}^1/_2k_3/\mathrm{KIE}) \tag{6d}$$

$$\mathbf{1e}/\mathrm{Mn}^+:\quad I_{\mathrm{H_2O}}/I_{\mathrm{HDO}} = (k_1 + k_2 + {}^1/_2k_3 + k_4)/({}^1/_2k_3/\mathrm{KIE}/\mathrm{SE}) \tag{6e}$$

A simple least-squares fit of the parameters in eqs 6a−6e gives $k_1 = 0.21 \pm 0.02$, $k_2 = 0.00 \pm 0.01$, $k_3 = 0.76 \pm$

Scheme 4. Newman Projections of the Insertion Intermediate 2d along the C(2)−C(3) Bond Provide an Explanation for the Increased Relative Amount of HDO Loss from This Diastereomer: (i) Formation of H_2O Involves a Less Favorable Gauche Arrangement, and (ii) HDO Loss Leads to the More Stable *trans*-2-Butene Complex



0.02, $k_4 = 0.03 \pm 0.01$, SE = 1.13 ± 0.04, and KIE = 1.51 ± 0.07. The small, but experimentally clearly significant stereochemical effect can be explained via Newman projections of the intermediates (Scheme 4).

This example may thus illustrate how systematic labeling studies can provide detailed insight into the regio- and even stereochemical bond activations of organic molecules by ionic metal ions in the gas phase. While the strategy is very widely applicable and at least for reasonably simple molecules not too demanding, it is not applied very often, because the required systematic sets of labeled compounds (e.g., Chart 1) are not commercially available and thus demand an independent preparative organic synthesis.[22]

3. Experimental Methods for the Investigation of Metal−Ion Reactions

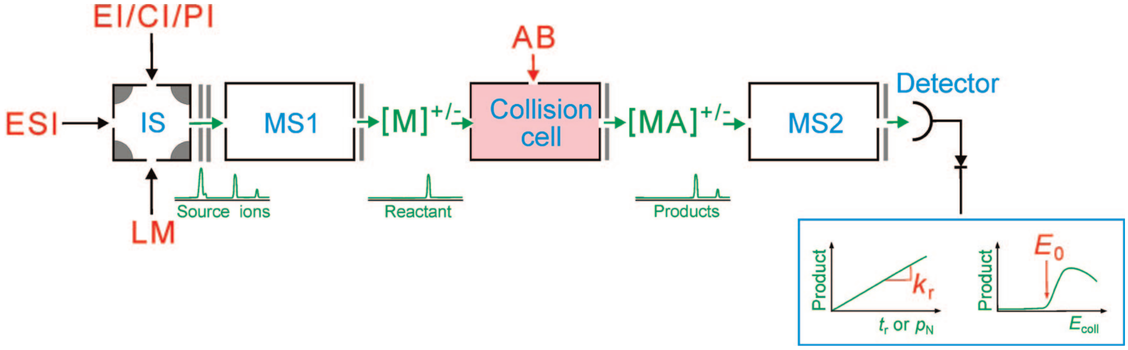
Almost any experimental method suitable for the investigation of the gas-phase reactions can be adapted to the examination of transition-metal ions with by and large any substrate. Therefore, we summarize the general principles rather briefly and instead focus on the particularities of metal-ion studies. The key components of such instrumentation are an ion source in which the species of interest with a given charge state are prepared from appropriate precursor(s), a device for the mass-selection of a primary reactant ion, the transformation of the primary ion into different species by unimolecular processes or interaction with photons, reactive or inert gases at thermal or higher collision energies, and the mass analysis as well as detection of the ions formed. Various types of mass analyzers exist in which the mass-selection steps are either separated in space or time and the various devices can also be combined.

Instead of dwelling upon further details, here it may suffice to state that with modern tandem mass spectrometers (Chart 2) scientists nowadays have the same instrumentation available at a molecular level as their synthetic colleagues in the laboratory: the ion source and the first mass analyzer correspond to the preparation and purification of a reactive species; mixing of this species with a neutral reagent in a collision cell at variable conditions (time, pressure, energy, etc.) is equivalent to the chemist's flask in a preparative laboratory the second mass analyzer together with the detector serve for the purification and characterization of the products being formed. Besides the lack of any effects of the environment (solvent, counterions, aggregation, etc.), which is not a limitation but one of the goal of gas-phase experiments, two major differences between the macroscopic world of laboratory synthesis and microscopic studies in a mass spectrometer are to be pointed out: (i) The absence of solvation as well as the nonexisting coupling to a thermal bath lead to much more reactive species and much faster reactions in the idealized gas phase, which is in part compensated by much shorter reaction times but is to be taken into account in comparisons. (ii) The amount of species handled largely differs, i.e. at least about 1 μmol in synthesis (10^{18} molecules), whereas gaseous ion experiments are typically limited to about 10^6 charged species. Hence, despite the frequent proposals of synthetic colleagues, it is hardly realistic to resolve more difficult structural problems in the products (e.g., stereochemistry) by other methods than mass spectrometry, such as NMR, by a recovery of the products from the prepumps of the mass spectrometer.[21]

The major methods which have been and are used for investigations of the bimolecular reactions of metal ions in the gas-phase are briefly described in the following.

(i) *Metastable ions.* Most of the earlier studies on metal-mediated C−H- and C−C-bond activation of alkanes were based upon unimolecular dissociations of metastable transition-metal ion complexes. Typically, the ions are generated via conventional chemical ionization (CI) and mass-selected,

Chart 2. Sketch of the Setup of a Tandem Mass Spectrometer for the Investigation of Ion/Molecule Reactions[a]



[a] In the ion source (IS, left), various means of ionization (EI, electron ionization; CI, chemical ionization; PI, photoionization; LM, various laser-based methods; ESI, electrospray ionization) provide a mixture of precursor ions, of which one particular anion or cation, $[M]^{\pm}$, is selected by the first mass analyzer (MS1), and transferred to a collision cell in which it can react with a neutral reagent, AB, for variable times at different reagent pressures and collision energies, and the precursor ion as well as the ionic product(s), here $[MA]^{\pm}$, are analyzed by means of MS2 and detected. The product yields as a function of either reaction time (t_r), reagent pressure (p_N), or collision energy (E_{coll}) directly provide rate constants (k_r) and reaction thresholds (E_0). EI, CI, and PI require volatile samples, ESI starts from solution, and LM are applied to solids. Note that, in ion-trapping techniques, the separation of mass-selection, reaction, and mass-analysis occurs in the time domain rather than in space.

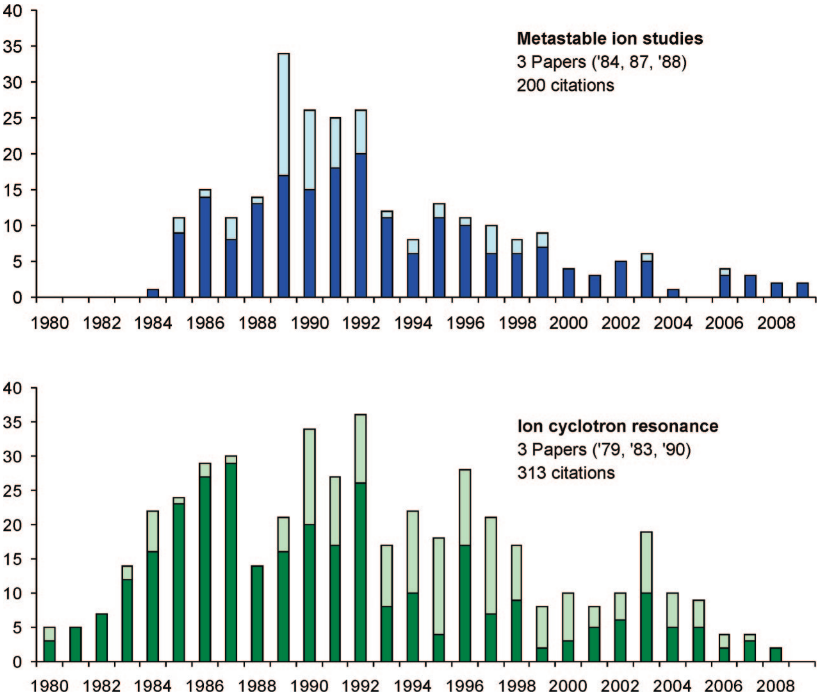


Figure 3. Average number of citations of key papers about metal-mediated C−H bond activation which can be associated with either metastable ion studies (method i) or ion-cyclotron resonance (method ii). Self-citations are indicated in lighter tones; three original papers from different research teams have been chosen in both areas; reviews were excluded.

and their unimolecular decay is monitored. The method is very precise, reproducible, and sensitive, but it lacks accuracy in that the energy content of the metastable ions is only very vaguely defined. Moreover, several instrumental conditions as well as the conception of the experiment itself very much limit the scope of the systems which can be studied; most significantly, for most transition metals, only oxidation states of limited importance are accessible, e.g. Fe^{I} rather than Fe^{II} and Fe^{III}. Further, ionic metal complexes generated from solution via electrospray ionization usually do not show any significant unimolecular decay because any excited species either already fragmented in the ionization region or underwent thermalization during transfer to the MS manifold and thus are not metastable anymore. Or, if expressed in the negative extreme, chemical ionization of metal precursors in the presence of organic substrates yields organometallic complexes of unknown energy content and in irrelevant oxidation states.[23,24] Accordingly, this technique is only rarely applied nowadays, as may be illustrated by a bibliometric analysis of selected key references in this area. To this end, we have chosen three key publications of metastable ion studies[25] and three key references about C−H bond activations by metal ions using ion-cyclotron resonance (ICR).[26] Upon inspection of the two graphs in Figure 3, it becomes obvious that although the metastable ion studies of metal ions were introduced later in time, the climax of the citations occurred earlier (in relation to the first paper) and the present level of citations is lower than that for the ICR studies.[27]

(ii) *Trapping techniques.* The second method comprises all kinds of trapping techniques (e.g., Fourier-transform ion-cyclotron resonance (ICR),[28] linear or quadrupolar ion traps (QITs),[29] etc.) in which a precursor ion made by any ionization method is mass-selected and then interacted with a neutral reagent of interest at a known pressure for a variable time, followed by detection. These methods have meanwhile developed to very powerful and rapid tools for the investigation of ion/molecule reactions, and the references include numerous applications of these techniques to bare and ligated transition-metal ions. In contrast to metastable ion studies, these investigations addressing the (thermal or hyperthermal) bimolecular reactivity of metal ions can be applied to ions stemming from any kind of ion source (e.g., also “cold” sources such as ESI or FAB), and this technique has been and is widely used in the area of transition-metal chemistry in the gas phase. With respect to the different types of ion traps, for reactive transition-metal ions, the different operating pressures in ICR and QIT are to be considered, as they may lead to significant quantitative differences as far as product branching ratio and adduct formation is concerned, while the qualitative patterns (i.e., which products are formed) are the same in both regimes.[30] Moreover, trapping techniques are most suited for the investigations of consecutive reaction including complete catalytic cycles.[13]

(iii) *Guided-ion beam methods.* Closely related to (ii) is the guided-ion beam (GIB) technology essentially pioneered by P. B. Armentrout in the field of metal-ion chemistry.[31−33] In GIB, the mass-selected precursor ions are allowed to react with a neutral reaction partner at well-defined conditions as a function of collision energy. While the GIB technique can also be applied for thermal ion−molecule reactions, its major power lies in the investigation of endothermic reactions. For illustration, we consider the hypothetical competition of reactions 7 and 8 as an example.

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \qquad (7)$$

$$M^+ + CH_4 \rightarrow MCH_3^+ + H \qquad (8)$$

While reaction 7 occurs at thermal conditions for several 5d metal cations (e.g., Pt^+, see above), both reactions are endothermic for 3d and 4d transition-metal cations. Consequently, only the reactant M^+ is observed at low collision energies in the GIB experiment. At elevated energies, conversion of kinetic into potential energy can override the

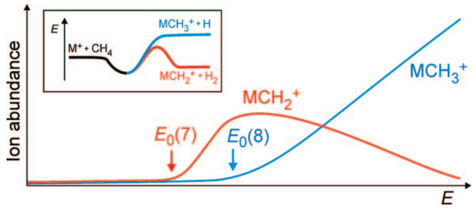


Figure 4. “Gedankenexperiment” for the competing channels in the C−H bond activation of methane by a metal cation M^+ according to reactions 7 and 8 to yield a metal−carbene cation (red) or a metal−methyl cation (blue) with the associated threshold energies $E_0(7)$ and $E_0(8)$, respectively. The inset shows the corresponding hypothetical potential-energy surface. Because the barrier for MCH_2^+ formation is above the energy of the reactants, it determines the overall yield of reaction 7, which leads to kinetic control. In contrast, simple C−H bond cleavage in reaction 8 is associated with thermodynamic control. Due to the entropic restrictions associated with kinetic control, the thermodynamically controlled reaction 8 wins over reaction 7 at larger energies, although it has a higher threshold energy.

endothermicities/kinetic barriers and hence leads to product formation (Figure 4).

To a first approximation, the experimentally observed onsets of the ionic products MCH_3^+ and MCH_2^+ correspond to the energy thresholds of reactions 7 and 8, respectively. In the case of a simple C−H bond cleavage as in reaction 8, thermodynamic control seems likely, such that the measured threshold energy $E_0(8)$ is a direct measure for the bond energy $D(M^+{-}CH_3)$, eq 9.

$$E_0(8) = D(H - CH_3) - D(M^+ - CH_3) \qquad (9)$$

In the case of reaction 7, however, operation of a kinetic barrier is likely to occur such that the experimental threshold is either a measure for the bond energy of the resulting MCH_2^+ ion (thermodynamic control) or a measure for the barrier height relative to the precursor ion (kinetic control); a decision can be made either by comparison of different reagents, yielding the same product ion at different thresholds, or by complementary computational studies of the potential energy surface with explicit inclusion of the barrier heights.[34]

Over the years, the Armentrout group has developed sophisticated methods for the determination of accurate energy thresholds from GIB measurements of endothermic reactions.[35] Nowadays, the thermodynamic quantities determined by this group and related teams using similar methods[36] form a solid database for the thermochemistry of gaseous metal ions.[37] In addition to the valuable thermochemical information derived from the reaction onsets, the shapes of the product-ion yields as a function of collision energy can provide very useful mechanistic insight with respect to the competition of the various channels.[38]

(iv) *Selected ion flow tube.* The major difference of selected ion flow tube (SIFT) experiments from other mass spectrometric studies is the pressure in the reaction zone. In a SIFT setup, ion generation and mass-selection are done in a conventional way, with the latter usually having quadrupoles. Then, the ion beam is injected into a flow tube with a rapid stream of a (light) carrier gas, usually helium, at a pressure of the order of about 1 mbar. At such a high pressure, the ions are immediately and without any serious doubt equilibrated with the temperature of the carrier gas. From the reaction region, the ions are extracted again and then analyzed with conventional means. Due to its warranty of thermalization in conjunction with the straightforward determination of the absolute pressure in the interaction region, the SIFT technology represents the ideal method to obtain benchmarks for kinetic measurements with other methods for the investigation of thermal ion/molecule reactions.[39]

The SIFT technique is primarily used for proton-transfer mass spectrometry and applications in atmospheric chemistry, while it has only occasionally been used for metal ions. In 2000, however, the Bohme group combined a SIFT setup with an inductively coupled plasma (ICP) source, which largely simplified the generation of metal ions directly from aqueous solution and independent of the metal’s volatility.[40] Since then, the Bohme team has published several of the most comprehensive screenings of the reactions of not just a few but almost all atomic metal ions with a variety of neutral reagents.[41,42]

With respect to ion generation, all methods can be used for metal ions, with the currently most important methods being variants of laser desorption[43] and electrospray ionization (ESI).[44] A drawback is, however, that many transition-metal compounds have a negative influence on instrument performance due to the deposition of semiconducting or insulating oxide layers on the ion optics, which accumulate static charge upon exposure to the ion beam. Moreover, volatile metal compounds can seriously and irreversibly deteriorate the performance of photomultiplier detection systems. The latter aspect has so far also seriously limited photoionization studies of transition-metal compounds using synchrotron radiation, although these experiments can provide highly valuable, absolute benchmarks for theory as well as other experiments. In the case of trimethoxo vanadium oxide, $OV(OCH_3)_3$, for example, the ionization energy of the neutral compound and the barrier height for loss of formaldehyde from the cation radical via β-H transfer were determined by synchrotron measurements.[45] In combination with complementary thermochemical data, these results were used for anchoring of the theoretical thermochemistry of $OV(OCH_3)_3^+$ from the cation radical all the way down to the quasi-terminal fragments VO^+ and VOH^+ (Figure 5).[46,47] Recently, Metz and co-workers have adapted their synchrotron experiments for the photoionization of mononuclear transition-metal compounds, such as the diatomic oxides FeO,[48] CuO,[49] and PtO.[50] In a few cases, more sophisticated photoionization schemes have also been applied to alkane activation by transition-metal ions.[51]

Electrospray ionization has not only widely contributed to biological chemistry but also significantly influenced the development of inorganic chemistry in general and of catalyst research in particular. In fact, many larger metal complexes whose generation as gaseous ions was impossible to think of only a few years ago are nowadays often tasks of minutes or hours. In the context of the time-honored cytochrome P450, for example, the transfer of model metal porphyrins into the gas phase via laser evaporation or sputtering methods gave poor ion currents and instable signals,[52] while this is straightforward with ESI,[53] and it even works for the biologically relevant core species.[54] In addition to the sampling of preformed ionic species from solution, a major feature of ESI is the ability to generate solvated ions in a controlled manner, thereby assisting in closing the gap between idealized studies in the gas phase and real chemistry in condensed media.[55,56] In the last few years, it has also been found that ESI, known and developed as a soft ionization method,[44] can also be modified to rather hard

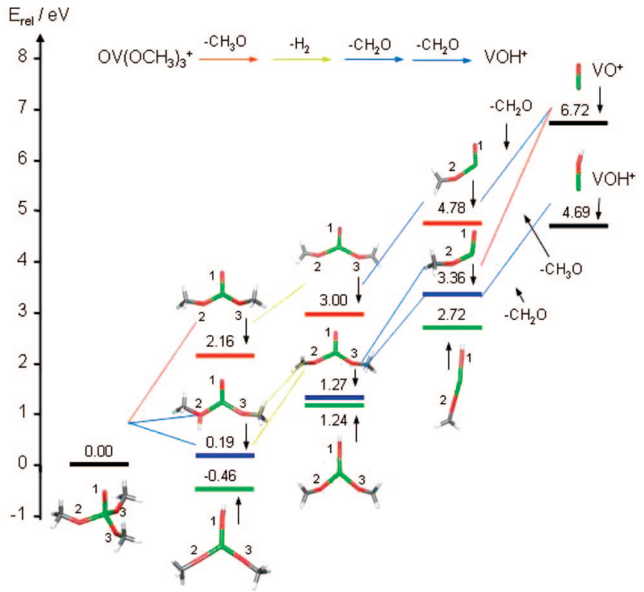


Figure 5. Thermochemistry of $OV(OCH_3)_3$ from the neutral compound via the cation $OV(OCH_3)_3^+$ all the way to the quasi-terminal fragments VO^+ and VOH^+. The computational predictions in the center of the diagram are backed-up with the matching side parts corresponding to either the ionization energy of intact $OV(OCH_3)_3$ determined via synchrotron ionization (left) or the heats of formation of diatomic VO^+ as well as VOH^+ on the right side.[46]

conditions of ionization, which can be used to efficiently produced highly reactive species,[57,58] including a broad variety of transition-metal cluster ions via excessive fragmentation of suitable polynuclear precursors.[59]

4. Alkane Activation by Transition-Metal Ions: Experimental Work

This section gives a summary of the experimental studies of alkane activation by neutral and ionic transition-metal species in the gas phase. Due to the fact that selectivity either has not been a relevant issue at all in these studies or it was not considered in detail, we briefly describe very few of these studies in more detail in order to illustrate several conceptual aspects, while the majority of the reactions are summarized in the form of tables. A few selected examples which also provide more detailed information about the selectivity of C−H bond activation are discussed in more detail in section 6. For the sake of readability, we further distinguish three different kinds of mononuclear metal species, i.e. (i) bare metal atoms, (ii) small metal compounds, such as oxides, halides, etc., and (iii) complex species with more than one, different, and large ligands which more closely resemble catalytically active species in the condensed phase.

4.1. Atomic Transition-Metal Cations

While 3d and 4d transition-metal cations M^+ cannot activate the C−H bonds of methane at thermal energies, several 5d metals dehydrogenate methane to afford the corresponding metal−carbene cations (for the case of platinum, see reaction 2). The mechanism of this reaction involves an initial insertion of the metal into one of the C−H bonds of methane followed by an α-hydrogen transfer (formal 1,1-elimination), which can lead either to a dihydrido intermediate, $(H)_2MCH_2^+$ (**3**, red), or directly to a dihydrogen complex, $(H_2)MCH_2^+$ (**4**, blue), from which molecular hydrogen is lost to afford the MCH_2^+ product (Scheme 5).

Scheme 5. Schematic Mechanisms for the M^+-Mediated Dehydrogenation of Methane to the Corresponding Metal−Carbene Cation MCH_2^+

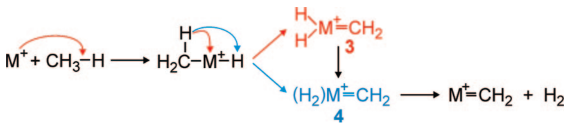


Table 2. Bond Dissociation Energies (in kJ mol^{-1}) of $M(C_2H_4)^+$ Complexes (Updated Compilation from Ref 62)[a]

Sc	134	Y	138	La	192
Ti	146[63]	Zr	146[64]	Hf	150
V	124[63]	Nb	148[65,66]	Ta	184
Cr	96[63]	Mo	127[67]	W	210
Mn	91[63]	Tc	109	Re	125
Fe	145[63]	Ru	149	Os	188
Co	186[63]	Rh	129	Ir	234
Ni	177[63]	Pd	93	Pt	230[68]
Cu	176[63]	Ag	141	Au	288

[a] No data found for Zn, Cd, and Hg.

Note that, in the course of the reaction, the formal oxidation state of the metal changes from M(I) in the atomic cation to M(III) in the metal−carbene cation; hence, only metals which are able to undergo such changes of the oxidation state can at all afford MCH_2^+ species. Further, for the occurrence of methane dehydrogenation to the carbene under thermal conditions, the bond strength $D(M^+-CH_2)$ must exceed the heat of dehydrogenation of methane (eq 10).[60]

$$CH_4 \rightarrow CH_2 + H_3$$
$$\Delta_r H = (465.0 \pm 0.9)\ \text{kJmol}^{-1}\ (4.19 \pm 0.01\ \text{eV}) \quad (10)$$

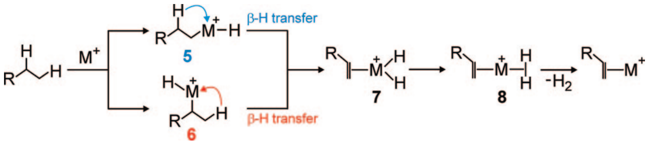
In addition to the mere thermodynamic requirements, occurrence of both the insertion step and the formal 1,1-elimination might be associated with significant kinetic barriers.

$$M^+ + R-CH_2CH_3 \rightarrow M(RC_2H_3)^+ + H_2 \quad (11)$$

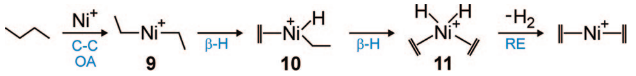
For all alkanes other than methane, dehydrogenation via a formal 1,1-elimination is negligible,[61] and most often a formal 1,2-dehydrogenation to the corresponding olefin complex (reaction 11) takes place instead. Note however that the reaction might be accompanied by reversible steps such that scrambling processes might occur, as recognized upon investigation of labeled substrates (see below). In the overall thermochemical balance, reaction 11 is exothermic when the bond energy of the cationic metal olefin complex, $D(M^+-RC_2H_3)$ exceeds the heat of hydrogenation of the olefin (typically 90−130 kJ mol^{-1}), which is the case for almost all cationic transition-metal olefin complexes, as shown in Table 2 for ethylene (R = H).

Mere exothermicity is, however, not sufficient for the occurrence of reaction 11 because also the kinetic barriers involved must be sufficiently low. These particular conditions are one of the key advantages of gas-phase ion chemistry because any bimolecular reactions can only occur if the entire pathway on the potential-energy surface of the reaction is lower in energy than the initial energy content of the reactants (both the thermal energy of the ions and the neutral reagent and additional kinetic energy of the ionic species).

Scheme 6. Schematic Mechanisms for the M^+-Mediated Dehydrogenation of an Alkane (R = H, Alkyl) with at Least Two Carbon Atoms to the Corresponding Metal−Olefin Complex $M(RC_2H_3)^+$



Scheme 7. Mechanisms for the Ni^+-Mediated Dehydrogenation of *n*-Butane as Proposed by Halle *et al.* in Ref 69



As far as the mechanism is concerned, already for the simple case of reaction 11 there exist two possible scenarios (Scheme 6). Either the initial insertion of the metal via oxidative addition involves a primary C−H bond of the terminal methyl group to yield intermediate **5** or insertion occurs into a secondary C−H bond of the methylene group to give **6**. From the insertion intermediates, the reaction can continue via β-hydrogen transfer (i.e., **5** → **7** and **6** → **7**) to the common dihydrido species **7**, which then, via reductive elimination, can interconvert into the dihydrogen complex **8** followed by liberation of H_2. The mechanistic picture shown in Scheme 6 was based on classical concepts of organometallic chemistry and has been used for long time, even though not all experimental results were consistent with the scheme, particularly with respect to structure **7**. In the mid-1990s, the strong boost provided by the development of density functional theory (DFT) has then shown that for many transition-metal ions structure **7** in fact is nonexistent and instead the reaction occurs directly from **5** and **6**, respectively, to **8** via multicentered transition structures, as detailed in section 5.

In addition to 1,2-elimination, several specific C−H bond activations by bare metal ions have been reported. Particularly interesting in this respect is the selective 1,4-dehydrogenation of *n*-butane by gaseous Ni^+ to afford a $[NiC_4H_8]^+$ cation.[69] Based on labeling data and comparative reactivity studies with $[NiC_4H_8]^+$ ions generated from different precursors, Halle et al. could convincingly demonstrate that the Ni^+-mediated dehydrogenation of *n*-butane directly leads to the bisethylene complex $Ni(C_2H_4)^+$ via an initial insertion into the central C−C bond of *n*-butane followed by two β-hydrogen transfers (i.e., **9** → **10** → **11**) to yield a dihydrido intermediate from which molecular hydrogen is lost in the last step (Scheme 7). Notably, the 1,4-dehydrogenation occurs with high selectivity, as demonstrated by the exclusive loss of D_2 from regioselectively labeled [1,1,1,4,4,4-D_6]-*n*-butane. Further, Halle et al. could also show that no metallacyclopentane intermediate is involved in the reaction. From the compilation of all results, even a qualitative potential-energy surface was proposed, which still performs well in comparison to later, much more advanced studies,[70] except that the metal−hydrido species **10** and **11** do not exist as genuine minima (see below).

In many deuterium-labeling studies of the activation of hydrocarbons by gaseous metal ions, information about the regioselectivity of bond-activation processes occurring is difficult to achieve, however, because extensive H/D equilibration precedes product formation. Reversibility between the intermediates (e.g., **5** ⇆ **8** and **6** ⇆ **8** in Scheme 6 or **9** ⇆ **11** in Scheme 7) can account for these equilibration processes. An additional mechanism for loss of positional identity of the hydrogen atoms in the organic backbone of the cationic complexes is conceivable via occurrence of inner-sphere electron transfer, that is transfer of an electron from the alkyl ligand(s) to the metal, resulting in formal complexes of neutral metal-hydride fragments with carbenium ions, for which extensive Wagner−Meerwein rearrangements have been known for a long time.[71] Both processes often very much limit the mechanistic information which can directly be extracted from labeling experiments. As a consequence, the complex product patterns which also result from superimposed kinetic isotope effects (KIEs) often have not been analyzed in detail. Unless the product distribution is fully statistical, i.e. all information about the position of the initial isotope label is lost, microkinetic modeling can regain quite a bit of useful mechanistic information.[72]

The experimentally studied reactions of mass-selected bare transition-metal ions with alkanes are summarized in Table 3. In addition to the studies in gas-phase ion chemistry, we also include several papers from matrix-isolation spectroscopy and neutral beam techniques provided that sufficient information about the products formed is available; the latter restriction refers to experimental studies of reactive neutral species via laser-induced fluorescence, which is a very sensitive and specific method but provides no information whatsoever about the products. In contrast, C−H bond activations by electronically excited metal atoms (e.g., Be, Mg, Ca, Zn, Cd, Hg)[73] are not included in Table 3, because putative catalytic scenarios via these particular route are inherently coupled with photosensitized processes (Scheme 8) and are thus beyond the scope of this review.[74,75]

In addition to neutral platinum,[182,189,190] matrix-isolation techniques have demonstrated that also bare rhodium atoms can insert into the C−H bonds of methane at cryogenic temperatures.[161,191−193] The course of these reactions typically is as follows: Upon codeposition of the metal and methane in a rare-gas matrix, photolysis promotes insertion of the metal into the C−H bonds of methane to afford the corresponding insertion intermediate **12**, from which—at least for some metals—the dihydrido species **13** as well as the carbyne complex **14** are accessible in subsequent steps of photolysis (Scheme 9). The structures of the species formed are then deduced via standard methods of matrix-isolation techniques, infrared spectroscopy in combination with isotopic labeling in particular.[194]

In most experimental studies of the reactions of neutral transition-metal atoms with small compounds, however, only the depletion of the reactants has been monitored, while the products themselves have not been detected; conclusions with regard to selectivity can thus only be indirect.[195,196] Activation of alkanes larger than methane has also been reported for several 4d metals, while most of the 4d metals only form adducts[197] and all 3d metal atoms do not react with alkanes.[85,198] Not surprisingly, bare metal dications are also able to activate alkanes and the examples known are included in Table 3,[199] but as very strong electrophiles, the reactivity of the metal dications is dominated by hydride-, alkanide-, or electron transfer reactions.[200] Recently, Marcalo et al. screened the entire series of lanthanide dications Ln^{2+} (Ln = La−Lu, except the radioactive Pm) and found an interesting correlation between the reactivity of these dications toward hydrocarbons and the difference $IE(Ln^+)$ − IE-

Table 3. Experimentally Studied Reactions of Anionic, Neutral, or Mono- or Dicationic, Bare Metal Atoms $[M]^{-/0/n+}$ with Alkanes (Denoted as Substrate), the Major Processes Observed, the Method Used, and the Year of Publication

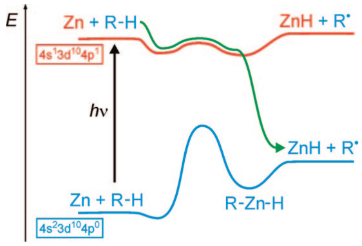
$[M]^{-/0/n+}$	substrate	process(es)[a]	method[b]	remarks	year
Al	CH_4	C−H	MIS	spontaneous	1983[76]
Al	CH_4	C−H	MIS	photoinsertion	1986[77]
M^+	CH_4	C−H, association	flow tube	59 metal cations	2009[78]
Al^+	CH_4, C_2H_6,	association	ICR		1996[79]
Sc	CH_4	C−H	MIS	photoinsertion	2006[80]
Sc^+	CH_4, C_2H_6	C−H, C−C	GIB	endothermic	1989[81]
Sc^+	C_2H_6	C−H	GIB		1987[82]
Sc^+	C_3H_8	C−H, C−C	GIB		1990[83]
Sc^+	C_2−C_4 alkanes	C−H, C−C	GIB		1985[84]
Sc^+−Zn^+	C_2H_6	C−H, C−C	flow tube	association	1986[85]
Sc^+−Zn^+	c-C_6H_{12}	C−H, C−C	ICR	diastereoselectivity	1995[86]
Ti	CH_4	C−H	MIS	photoinsertion	2004[87]
Ti^+	CH_4	C−H	GIB		1988[88]
Ti^+	C_2H_6	C−H	MI		1997[89]
Ti^+	C_2−C_4 alkanes	C−H, C−C	GIB		1989[90]
Ti^+	C_2H_6, C_3H_8	C−H	flow tube		1996[91,92]
Ti^+	C_3H_8	C−H	MI, GIB	labeling	1998[93]
Ti^+	C_2−C_6 alkanes	C−H, C−C	ICR		1982[94]
Ti^+	C_2−C_8 alkanes	C−H, C−C	GIB	adduct lifetimes	1986[95]
Ti^{2+}	C_1−C_3 alkanes	C−H, ET	flow tube	$TiCH_2^{2+}$ from CH_4	1986[96]
V	CH_4	C−H	MIS	photoinsertion	2006[97]
V^+	CH_4	C−H	GIB	endothermic	1987[98]
V^+	C_2H_6	C−H	REMPI/TOF		1987[99]
V^+	C_2H_6	C−H	MI		1997[89]
V^+	C_2H_6, C_3H_8	C−H	REMPI/TOF	state selective	1990[100]
V^+	C_3H_8	C−H	MI, GIB	labeling	1998[93]
V^+	C_2−C_6 alkanes	C−H, C−C	ICR	secondary reactions	1986[101]
Cr^+	CH_4	C−H	GIB	excited state	1981[102]
Cr^+	CH_4	C−H	GIB	endothermic	1988[103]
Cr^+	C_2H_6	C−H, C−C	GIB	endothermic	1989[104]
Cr^+	C_3−C_5 alkanes	C−H, C−C	GIB	labeling	1992[105]
Cr^+	alkanes	n.r.	ICR		1988[106]
Mn	CH_4	C−H	MIS	photoinsertion	1980[107]
Mn	CH_4	C−H	MIS	photoinsertion	1984[108]
Mn^+	C_2H_6	C−H, C−C	GIB	endothermic	1989[109]
Mn^+	C_4H_{10}, C_5H_{12}	C−H, C−C	GIB	endothermic	1990[110]
Fe	C_1−C_3 alkanes	C−H	MIS	photoinsertion	1980[107,108,111]
Fe^+	CH_4	C−H	GIB	endothermic	1996[34a,112]
Fe^+	C_1−C_3 alkanes	C−H, C−C	GIB	CH_4, C_2H_6: endothermic	1988[113]
Fe^+	C_1−C_4 alkanes	C−H, C−C	flow tube	CH_4, C_2H_6: n.r.	1997[114]
Fe^+	C_2H_6	C−H, C−C	GIB	endothermic	1992[115]
Fe^+	C_2−C_6 alkanes	C−H, C−C	ICR		1982[94]
Fe^+	C_3H_8	C−H, C−C	GIB		1987[116]
Fe^+	C_3H_8	C−H, C−C	MI, GIB	labeling	1994[117]
Fe^+	C_3H_8, C_4H_{10}	C−H, C−C	REMPI/TOF	state selective	1990[118]
Fe^+	C_3H_8	C−H, C−C	IM-MS	state selective	1992[119]
Fe^+	alkanes	C−H, C−C	ICR		1983[26b,120]
Fe^+	C_3−C_8 alkanes	C−H, C−C	GIB	labeling	1983[121]
Fe^+	n- and i-C_4H_{10}	C−H, C−C	ICR		1979[26a]
Co	CH_4	C−H	MIS	photoinsertion	1980[107,122]
Co^+	CH_4	C−H	GIB	endothermic	1995[123,124]
Co^+	C_2H_6	C−H, C−C	GIB		1996[125,126]
Co^+	C_2−C_5 alkanes	C−H, C−C	GIB		1989[127]
Co^+	C_3H_8	C−H, C−C	MI, GIB		1990[128]
Co^+	C_3H_8	C−H, C−C	MI, GIB	labeling	1991[129]
Co^+	C_3H_8	C−H, C−C	GIB		1996[130,131]
Co^+	C_3H_8	C−H, C−C	IM-MS	state selective	1992[119]
Co^+	C_4−C_6 alkanes	C−H, C−C	MI	kinetic energy release	1988[25c]
Co^+	alkanes	C−H, C−C	GIB		1983[132]
Co^+	alkanes	C−H, C−C	ICR		1983[120]
Co^+	C_3−C_8 alkanes	C−H, C−C	GIB	labeling	1983[121]
Co^+	butanes	C−H, C−C	ICR		1984[133]
Co^+	butane	C−H, C−C	crossed beam		2000[134]
Co^+	isobutane	C−H, C−C	crossed beam		2002[135]
Co^+	cyclopentane	C−H, C−C	MI		1990[136]
Co^+	cyclohexane	C−H	ICR	also $Co_m(CO)_n^+$	1991[137]
Ni	CH_4	C−H	MIS	photoinsertion	1988[138]
Ni^+	CH_4	C−H	GIB + theory	endothermic	2005[34b]
Ni^+	C_2H_6	C−H	REMPI/TOF		1994[139]
Ni^+	C_3H_8	C−H, C−C	MI, GIB	labeling	1994[117]
Ni^+	C_3H_8	C−H, C−C	REMPI/TOF	theory	1998[140]
Ni^+	C_3−C_6 alkanes	C−H, C−C	GIB + ICR	labeling	1982[69]
Ni^+	alkanes	C−H, C−C	ICR		1983[120]
Ni^+	C_3−C_8 alkanes	C−H, C−C	GIB	labeling	1983[121]
Ni^+	C_4−C_6 alkanes	C−H, C−C	MI	kinetic energy release	1988[25c]
Ni^+	n-C_4H_{10}	C−H, C−C	REMPI/TOF	labeling, theory	1999[70]
Cu	CH_4	C−H	MIS	photoinsertion	1980[107,141]

Table 3. Continued

$[M]^{-/0/n+}$	substrate	process(es)[a]	method[b]	remarks	year
Cu^+	alkanes	association	GIB		1987[142]
Cu^+	c-C_6H_{12}	association	GIB		1994[143]
Zn	CH_4	C−H	MIS	photoinsertion	1980[107]
Zn^+	C_1-C_5 alkanes	C−H, C−C	GIB	endothermic	1986[144]
Ga	CH_4	C−H	MIS	photoinsertion	1983[76]
Y	CH_4	C−H	MIS	photoinsertion	2007[80]
Y^+	C_1-C_6 alkanes	C−H, C−C	ICR		1987[145]
Y^+	CH_4, C_2H_6	C−H, C−C	GIB	endothermic	1989[81]
Y^{2+}	C_1-C_6 alkanes	C−H, C−C, ET	ICR	CH_4: n.r.	1997[146]
Zr	CH_4	C−H	MIS	photoinsertion	2005[147]
Zr	C_4-C_5 alkanes	C−H	other	spontaneous	1979[148]
Zr^+	CH_4	C−H	GIB + theory		2003[34c,149]
Zr^+	C_2H_6, C_3H_8	C−H, C−C	GIB	also c-C_3H_6	2003[150]
Zr^{2+}	C_1-C_5 alkanes	C−H, C−C, ET	ICR	methane oligmerization	1991[151]
Nb	CH_4	C−H	MIS	photoinsertion	2006[97]
Nb^+	C_1-C_7 alkanes	C−H, C−C	ICR		1989[152]
Nb^+	C_1-C_3 alkanes	C−H, C−C	GIB		2000[34xx]
Nb^{2+}	C_1-C_4 alkanes	C−H, C−C, ET	ICR		1987[153]
Mo	CH_4, C_2H_6	C−H	crossed beam	endothermic	2000[154]
Mo	CH_4	C−H	MIS	photoinsertion	2005[155]
Mo^+	CH_4	C−H	GIB + theory	endothermic	2006[34e]
Mo^+	C_2H_6, C_3H_8	C−H, C−C	GIB + theory	endothermic	2007[67,156]
Mo^+	C_1-C_4 alkanes	C−H	ICR	$\leq C_3$: n.r.	1992[157]
Mo^+	alkanes	C−H, C−C	ICR		1988[106]
Tc^+	alkanes	C−H, C−C	ICR		2004[15,158]
Ru^+	C_2-C_4 alkanes	C−H, C−C	GIB		1999[159]
Ru^+	C_1-C_5 alkanes	C−H, C−C	GIB		1986[160]
Rh	CH_4	insertion	MIS + theory	cryogenic T	2005[161]
Rh^+	CH_4	C−H	GIB		1995[124a,162]
Rh^+	C_2H_6, C_3H_8	C−H, C−C	GIB		1995[163]
Rh^+	C_1-C_8 alkanes	C−H, C−C	ICR		1982[164]
Rh^+	C_1-C_5 alkanes	C−H, C−C	GIB		1986[160]
Pd^+	C_1-C_3 alkanes	C−H, C−C	GIB	CH_4, C_2H_6: endothermic	1997[34f]
Pd^+	C_1-C_5 alkanes	C−H, C−C	GIB		1986[160]
Ag	CH_4	C−H	MIS	photoinsertion	1980[107]
Ag^+	C_2-C_4 alkanes	C−H, C−C	GIB	endothermic	1995[165]
Ag^+	alkanes	association	GIB		1987[142]
La	CH_4	C−H	MIS	photoinsertion	2007[80]
La^+	CH_4, C_2H_6	C−H, C−C	GIB	endothermic	1989[81]
$M(5d)^+$	CH_4	C−H	ICR	M = La−Au	1991[5a,b]
$La^{+/2+}$	C_1-C_4 alkanes	C−H, C−C, ET	ICR	CH_4, C_2H_6: n.r.	1992[166]
Ln^+	C_1-C_4 alkanes	C−H, C−C	ICR	M = Pr, Eu, Gd	1988[167]
Ln^+	C_1-C_6 alkanes	C−H, C−C	ICR	reactivity screening	1995[15]
Ln^+	c-C_6H_{12}	C−H, C−C	TOF		2005[168]
Ln^{2+}	C_1-C_6 alkanes	C−H, C−C	ICR		2008[169]
Er^+	CH_4	association	IM-MS	multiple collisions	2005[170]
Lu^+	CH_4, C_2H_6	C−H, C−C	GIB	endothermic	1989[81]
Hf	CH_4	C−H	MIS	photoinsertion	2005[171]
Hf^+	CH_4	C−H	GIB + theory	endothermic	2006[34g]
Ta	CH_4	C−H	MIS	photoinsertion	2006[97]
Ta^+	CH_4	C−H	ICR		1995[172]
Ta^+	CH_4	C−H	GIB + theory		2007[34h,151]
Ta^+	C_1-C_7 alkanes	C−H, C−C	ICR		1989[152]
Ta^{2+}	CH_4	C−H, ET	GIB		2008[173]
Ta^{2+}	C_1-C_5 alkanes	C−H, ET	ICR	ET for $\geq C_2$	1991[151]
W	CH_4	C−H	MIS	photoinsertion	2005[174]
W^+	C_2-C_9 alkanes	C−H, C−C	ICR		1994[175]
W^+	C_1-C_6 alkanes	C−H, C−C	ICR	labeling	1997[176]
W^+	CH_4	C−H	GIB + theory	oligomerization	2006[34i]
Re^+	CH_4		GIB + theory	endothermic	2004[34j,177]
Os^+	CH_4	C−H	ICR		1989[178]
Os^+	cycloalkanes	C−H, C−C	ICR		1995[179]
Ir^+	CH_4	C−H	GIB + theory	dihydrido intermediate	2006[34k,180]
Pt^-	CH_4	C−H	ICR		2000[9a,181]
Pt	CH_4	C−H	others		1991[182]
Pt^+	CH_4	C−H	ICR		1991[5a−f]
Pt^+	CH_4	C−H	GIB		2001[5g]
Au	CH_4	C−H	MIS	photoinsertion	1980[107]
Au^+	CH_4	C−H	GIB + theory	endothermic	2006[34m]
An^+	C_1-C_4 alkanes	C−H, C−C	ICR	An = Th, Pa, U, Np, Pu, Am, Cm	2007[183,184]
Th	CH_4	C−H	MIS	photoinsertion	2005[185]
Th^+	C_1-C_4 alkanes	C−H	ICR		1996[186]
U^+	CH_4	C−H	ion beam	endothermic	1977[187]
U^+	C_1-C_4 alkanes	C−H, C−C	ICR		1995[188]

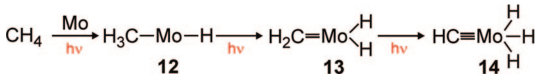
[a] C−H, C−H bond activation; C−C, C−C bond activation; ET, electron transfer; n.r., no reaction. [b] GIB, guided ion beam; ICR, ion-cyclotron resonance; IM-MS, ion-mobility mass spectrometry; MI, metastable ion studies; MIS, matrix isolation spectroscopy; REMPI, resonance-enhanced multiphoton ionization; TOF, time-of-flight mass spectrometry.

Scheme 8. Simplified Scheme for the Bond Activation of an Alkane R−H by Electronically Excited Metal Atoms Using Atomic Zinc with the Valence Configurations $4s^2 3d^{10} 4p^0$ (Ground State, Blue) and an Excited $4s^1 3d^{10} 4p^1$ State (Red) as an Example[a]



[a] The green arrow indicates the post-photoexcitation course of the net reaction from the excited to the ground-state surface.

Scheme 9. Consecutive Hydrogen Transfer upon Photoinduced Insertion of Atomic Mo into a C−H Bond of Methane (Adopted from Ref 193a)



(C_mH_n),[169] which is consistent with the reaction window theory for dication reactions.[200−202]

4.2. Small (Ionic) Metal Compounds

In comparison to bare metal atoms (and their ions), there is an important distinction to be made with respect to the same metals bearing additional ligands. As this conceptual aspect has been detailed recently,[203] it is presented only briefly here. A closed-shell ligand L, such as a carbonyl ligand, an olefin, phosphine, etc., *modifies the electronic situation* of the metal center by donation/backdonation and may additionally also impose some steric constraints. In marked contrast, an open-shell ligand X, such as a halogen, an OH group, a pseudohalogen, a cyclopentadienyl ligand, etc., not only bears the above influences but moreover leads to a different formal oxidation state of the metal and thus *completely changes the electronic situation*, including significant changes in thermochemistry, ionization, and recombination energies, as well as spin states. Accordingly, addition of a closed-shell ligand L may reflect the modulation of the metal ion's reactivity by the ligand, whereas M^+ and MX^+ should only be compared with detailed consideration of all consequences arising from the change of the formal valence state of the metal. An instructive and simple example in this respect are the bare metal ions M^+ (M = Cr and Fe) in comparison to their monocarbonyls $M(CO)^+$ and their monochlorides MCl^+. Thus, Cr^+ is the least reactive 3d metal cation, which can be attributed to the $4s^0 3d^5$ configuration of the $Cr^+(^6S)$ ground state imposing considerable barriers toward any changes of this favorable electronic situation; note that this also is reflected in the ethylene binding energies (Table 2). Consequently, Fe^+ is capable of activating many substrates, including hydrocarbons larger than ethane, whereas bare Cr^+ almost is inert. In terms of bond-activation processes, the carbonyl complexes $Cr(CO)^+$ and $Fe(CO)^+$ are even less reactive than the bare metals, as expected. In contrast, the monochloride $CrCl^+$ promotes C−H bond activation of alkanes, whereas $FeCl^+$ is completely inert in this respect. This observation therefore is not a mystery but instead a direct consequence of the consideration of the electronic properties of the metals. For this reason, from the still limited set of reactivity studies of ligated transition, no general guidelines can be drawn, while several trends are obvious and perfectly in line with the above consideration that the change of the formal valence state has a crucial influence on the metal's reactivity, even more than the charge state itself has.

As an illustration of these aspects, we refer to the activation of methane—the obviously most challenging substrate—by ligated transition-metal cations MX^+.[204] As shown in Table 3, some of the 5d metal ions are capable of activating methane under thermal conditions, while none of the 3d and 4d metal cations does. In marked contrast, a variety of 3d and 4d metal cations with a single, monovalent ligand bring about the activation of methane. In addition to the substantial consequences of the formal oxidation state, there exist yet another important aspect in this context, because in almost all of the cases known so far, the covalent ligand X is actively involved in bond formation, as demonstrated by the release of neutral HX as a product; quite obviously, the bond strength D(H−X) is thus—among others—a particularly decisive parameter for the reactivity of such metal species.

Among the examples given in Table 4, in which metal oxides are excluded, we select three classes of covalent MX^+ species for a brief more detailed discussion. While the M^+ ions with M = Fe−Ni do not react with methane, the corresponding metal hydrides MH^+ are much more reactive and NiH^+, for example, reacts quite efficiently with methane to generate $NiCH_3^+$, concomitant with molecular hydrogen (Table 4). Likewise, the degenerate ligand exchange of MCH_3^+ cations with methane has been investigated for the late transition metals Fe, Co, Ni, Ru, Rh, Pd, Ir, Os, and Pt by both experiment and theory.[205] The MCH_3^+ cations of 3d metals are either unreactive or follow a σ-bond metathesis pathway, whereas the MCH_3^+ cations of the metals from the 4d and 5d series can also undergo sequences of oxidative addition and reductive elimination. When switching from X = H or CH_3 to significantly more electronegative ligands such as X = halogen or OH, another boost in reactivity is observed. Thus, $NiOH^+$ as well as the related $HNiOH^+$ cation react with methane under thermal conditions,[206,207] and an alkane-reactivity screening of the NiX^+ cations (X = F, Cl, Br, I) has shown the (expected) reactivity order F > Cl ≈ Br > I.[208] A further notable difference between these various covalent ligands is that with increasing electronegativity of X the tendency for formal hydride abstraction from the alkane to afford a carbenium ion increases as well. While it goes without saying that the latter depends on the stability of the carbenium ion (i.e., nonoccurrence in the case of methane, large probability for isobutane), the trends along the series of X can be understood by increasing the positive charge of the metal center when ligated to more electronegative elements (or groups). Not surprisingly, carbenium ion formation is thus most pronounced for X = F. Following the same line of reasoning, the trends upon increasing the number of fluoro ligands in CrF_n^+ cations ($n = 0 - 4$) can be explained: Cr^+ itself is unreactive, and despite a conceptually feasible influence of steric constraints, the reactivity increases from CrF^+ to CrF_4^+ with more and more preference for hydride and even electron transfer.[209]

As far as coordinative ligands L are concerned, one notes a general decrease in reactivity in the comparison of the bare metal cations M^+ with the ligated species $M(L)_n^+$. As detailed below, however, this decrease in reactivity often is associated with a significant increase in selectivity. In the case of

Table 4. Experimentally Studied Reactions of Small, Ligated Metal Ions $[\mathrm{M(L,X)}]^{\mp}$ with Alkanes (Denoted as Substrate), the Major Processes Observed, the Method Used, and the Year of Publication[a,b]

$[\mathrm{M(L,X)}]^{\mp}$	substrate	process(es)	method	comments	year
CpMg^+	C_1-C_4 alkanes	association	flow tube		2000[210]
$(\mathrm{CH_3})_2\mathrm{Sc}^+$	cycloalkanes	C−H	ICR		1996[211]
$(\mathrm{CH_3})_2\mathrm{Sc}^+$	C_1-C_5 alkanes	C−H	ICR	$\leq C_2$: n.r., labeling	1994[212]
$\mathrm{CrF}_n{}^+$	C_1-C_4 alkanes	C−H, C−C	ICR	$n = 0-4$	1998[209]
CrCl^+	C_4H_{10}	C−H	ICR		1986[213]
$\mathrm{M(CO)}_n{}^-$	n-C_7H_{14}	C−H	ICR	M = Cr−Fe, $n = 1-3$	1993[214]
MnCl^+	C_4H_{10}	n.r.	ICR		1986[213]
$\mathrm{Mn(CO)_3}^-$	C_1-C_4 alkanes	C−H	flow tube	CH_4: n.r.	1991[215]
FeH^+	C_1-C_4 alkanes	C−H	GIB	CH_4, C_2H_6: endothermic	1984[216]
FeH^+	CH_4	C−H	HPMS	T dep.	2004[217]
FeD^+	C_1-C_5 alkanes	C−H, C−C	ICR	CH_4, C_2H_6: n.r.	1983[218]
FeS^+	CH_4	C−H	GIB, ICR	endothermic, TSR	2001[219]
FeS^+	C_1-C_6 alkanes	C−H, C−C	ICR		1986[220]
FeOH^+	C_1-C_6 alkanes	C−H, C−C	ICR		1986[221]
FeCl^+	C_4H_{10}	n.r.	ICR		1986[213,222]
FeNH^+	C_1-C_4 alkanes	C−H, C−C	ICR		1998[223]
$\mathrm{FeCH_2}^+$	C_1-C_6 alkanes	C−H, C−C	ICR		1985[224]
$\mathrm{MCH_3}^+$	CH_4	C−H	GIB	M = Fe−Ni	2007[205]
$\mathrm{FeCH_3}^+$	C_1-C_6 alkanes	C−H, C−C	ICR		1984[225]
$\mathrm{FeCF_2}^+$	C_1-C_7 alkanes	C−H	ICR		1998[226]
$\mathrm{FeCF_3}^+$	C_1-C_7 alkanes	C−H	ICR	$\leq C_3$: n.r., CF_2 loss	1998[227]
$\mathrm{Fe(CO)_2}^-$	C_1-C_4 alkanes	C−H	flow tube		1991[215,228]
$\mathrm{Fe(L)}^+$	C_3H_8	C−H, C−C	GIB	L = CO, H_2O	1996[229]
$\mathrm{Fe(CH_2X)}^+$	C_1-C_6 alkanes	C−H, C−C	ICR	X = O, S	1997[230]
CoD^+	C_1-C_5 alkanes	C−H, C−C	ICR	CH_4: n.r.	1983[218]
CoS^+	C_1-C_6 alkanes	C−H, C−C	ICR		1986[220]
CoOH^+	C_1-C_6 alkanes	C−H, C−C	ICR		1986[221]
$\mathrm{CoCH_2}^+$	C_1-C_6 alkanes	C−H, C−C	ICR		1985[224]
$\mathrm{CoCH_3}^+$	C_1-C_6 alkanes	C−H, C−C	ICR		1984[225]
CpCo^+	CH_4	association	HPMS	T dep.	2003[231,232]
CpCo^+	C_2H_6	C−H	ICR	M = Fe: n.r.	1999[233]
CpCo^+	C_3H_8	C−H	others		2007[234]
CpCo^+	C_1-C_6 alkanes	C−H	ICR		1985[235]
$\mathrm{CoCH_2}^+$	C_1-C_6 alkanes	C−H, C−C	ICR		1985[224]
$\mathrm{CoCF_2}^+$	C_1-C_7 alkanes	C−H	ICR		1998[226]
$\mathrm{CoCF_3}^+$	C_1-C_7 alkanes	C−H	ICR	$\leq C_3$: n.r., CF_2 loss	1998[227]
NiH^+	CH_4	C−H	others	T dep.	2004[217]
NiH^+	CH_4	C−H	GIB		2007[206a]
NiD^+	C_1-C_5 alkanes	C−H, C−C	ICR		1983[218]
NiX^+	CH_4	C−H	GIB + theory	X = H, CH_3, OH, F	2008[206b]
NiX^+	C_1-C_4 alkanes	C−H, C−C	ICR	X = F−I	2007[208]
NiS^+	C_1-C_6 alkanes	C−H, C−C	ICR		1986[220]
HNiOH^+	CH_4	C−H	GIB		2007[206a]
CpNi^+	C_2H_6	C−H	ICR	M = Fe: n.r.	1999[233]
CpNi^+	C_3H_8	C−H	others		2007[233]
$\mathrm{MCH_3}^+$	CH_4	C−H	GIB	M = Ru−Pd	2007[205]
PdH^+	CH_4	C−H	GIB + theory		2007[236]
$\mathrm{W(CO)}_n{}^+$	C_1-C_3 alkanes	C−H	ICR	$n = 1-4$	1995[237]
$\mathrm{Re(CO)}_n{}^+$	cyclohexane	C−H	ICR		1987[238]
$\mathrm{MCH_3}^+$	CH_4	C−H	GIB	M = Os - Pt	2007[205]
PtX^+	CH_4	C−H	GIB	X = H, Cl, Br	2005[5h]

[a] For the definition of abbreviations, see footnotes of Table 3. [b] For metal oxides, see Table 5.

gaseous iron(I) cations, for example, it has been demonstrated that coordinative ligands can decisively influence the selectivity between C−H and C−C bond activation.[229,230,239] We return to this aspect further below in section 6 but may note already here that the general trend for decreased reactivity of ligated metal ions also has its exceptions and even a single rare-gas atom can in fact increase the efficiency of methane activation in the case of cluster ions (see section 7).

Examples for the activation of alkanes by transition-metal anions are scarce.[214,240,241] Outstanding examples in this respect are the two carbonyl complexes $\mathrm{Mn(CO)_3}^-$ and $\mathrm{Fe(CO)_2}^-$.[215] McDonald et al. found that among a variety of $\mathrm{M(CO)}_n{}^-$ ions (M = Cr, Mn, Fe; $n = 1-4$) only these two coordinatively unsaturated species are able to activate alkanes. Dehydrogenation occurs for all investigated alkanes in which a formal 1,2-elimination is possible, whereas under the flow-tube conditions applied, methane as well as neopentane only yield the formal adducts.[228] For the case of neopentane, a subsequent ion/molecule reaction with deuterium demonstrates the occurrence of C−H bond activation via oxidative addition (OA), in that the product ion undergoes a single H/D exchange (**15** → **15′**, Scheme 10), whereas no exchange at all would be expected for the mere association complex $\mathrm{Fe(C(CH_3)_4)(CO)_2}^-$.

4.3. Transition-Metal Oxides

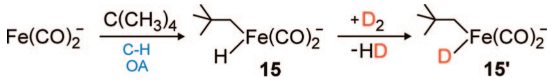
Due to their profound importance in the context of oxidation catalysis, the reactions of gaseous transition-metal oxide ions with hydrocarbon substrates have received particularly broad attention.[242] The high activity in this area is further related with the often exceptionally large reactivity of metal oxides on the one hand and the use of metal oxides as catalyst−support materials on the other. As far as

Table 5. Experimentally Studied Reactions of Metal-Oxo Species $[MO_m]^{0/n+}$ with Alkanes (Denoted as Substrate), the Major Processes Observed, the Method Used, and the Year of Publication[a]

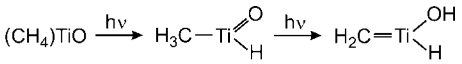
$[M]^{-/0/+}$	substrate	process(es)[b]	method	comments	year
MgO^+	CH_4	C−H	GIB + theory		2006[58a]
MO^+	CH_4	C−H	flow tube	M = Ca, Sr, Ba	2009[249]
Sc	CH_3OH	insertion	MIS + theory		2004[250]
TiO	CH_4	association	MIS + theory	photoinsertion	2006[244]
V^+	CH_3OH	O-abstraction	ICR + theory		2005[251]
VO^+	C_2-C_6 alkanes	C−H	ICR		1986[101,252]
VO_2^+	C_2H_6	C−H	ICR + theory		1999[19a,253]
VO_2^+	C_2-C_4 alkanes	C−H	ICR + theory		2003[19b]
CrO^+	C_2-C_4 alkanes	C−H	ICR		1986[254]
CrO_2^+	C_1-C_4 alkanes	C−H	ICR		2004[255,256]
MnO	CH_4	association	MIS + theory	photoinsertion	2004[257]
MnO^+	CH_4		ICR		1995[258]
FeO	CH_4	association	MIS + theory	photoinsertion	2004[258]
FeO^+	CH_4	C−H, O_T	ICR		1990[20c,259,260]
FeO^+	CH_4		MI	intermediates	1992[261]
FeO^+	CH_4	C−H, O_T	several		1997[262]
FeO^+	CH_4		others	intermediates	2002[48b]
FeO^+	CH_4	C−H, O_T	GIB		2007[58b]
FeO^+	C_1-C_6 alkanes	C−H, C−C, O_T	ICR		1984[20a]
$Fe(O)(OH)^+$	C_1-C_4 alkanes	C−H, O_T	ICR		1991[263]
CoO^+	C_1-C_5 alkanes	C−H, C−C, O_T	ICR		1994[264]
CoO^+	CH_4	C−H, O_T	GIB		1994[265]
Nb^+	CH_3OH	O-abstraction	ICR + theory		2005[251a]
NbO_n	CH_4	association	MIS	photoinsertion	2005[266]
MoO_n^+	C_1-C_4 alkanes	C−H, C−C	ICR		1992[157]
MoO_n^+	CH_4, C_2H_6	C−H	ICR	$n = 1-3$	1997[267,268]
LnO^+	C_1-C_4 alkanes		ICR	n.r.	1997[269]
CeO_2^+	C_1-C_4 alkanes	C−H	ICR		1996[270]
Ta^+	CH_3OH	O-abstraction	ICR + theory		2005[251a]
TaO_2	CH_4	association	MIS	photoinsertion	2005[266]
ReO_n^+	CH_4	C−H	ICR	$n = 2-6, 8$	2001[271]
OsO_n^+	CH_4	C−H	ICR	$n = 1-4$	1989[178,272]
PtO^+	CH_4	C−H	ICR		1997[5e]
PtO_2^+	CH_4, C_2H_6	C−H, C−C	ICR	nonselective	2001[13f]
AnO^+	C_1-C_4 alkanes	C−H	ICR	An = Th, Pa, U, Np, Pu, Am, Cm	2007[183,184]
ThO_n^+	C_1-C_4 alkanes	C−H	ICR	$n = 1, 2$	1997[269]
UO_n^+	C_1-C_4 alkanes	C−H	ICR	$n = 1, 2$	1997[269]

[a] For the definition of abbreviations, see footnotes of Table 3. [b] O_T stands for oxygen-atom transfer from the metal oxide to the substrate.

Scheme 10. C−H Bond of Neo-pentane by $Fe(CO)_3^-$ and Structural Proof via H/D Exchange



Scheme 11. Consecutive Photoactivation of the C−H Bonds of Methane by Neutral TiO at 10 K



reactivity is concerned, the cationic forms of high-valent transition-metal oxides are among the most powerful oxidizing agents so far studied in gas-phase experiments. The seemingly simple diatomic cation FeO^+, for example, activates all oxidizable substrates tested so far, including dihydrogen, methane, and benzene; only fully oxidized carbon compounds resist toward the FeO^+ cation, e.g. CO_2 and CF_4.[243] Further, metal-oxides are the most important class of substances in the context of the catalytic partial oxidation of methane, and as an example for fundamental studies, here we refer to a matrix isolation study of a TiO, a neutral oxide of an early 3d metal.

In elegant spectroscopic studies, neutral TiO was shown to be able to activate methane upon irradiation with visible light (Scheme 11).[244,245] Thus, only the mere adduct $(CH_4)TiO$ is formed at cryogenic temperatures, which can be rearranged to the insertion species $(CH_3)Ti(H)(O)$ via 500 nm photons. Further photochemical processes involve a rearrangement to $(CH_2)Ti(H)(OH)$, which can add a second methane molecule to afford $(CH_3)_2Ti(H)(OH)$. In comparison to most ionic species, in particular with respect to oxides of later transition metals, the C−H bond activation does not occur across the metal−oxygen bond but only takes place at the metal with the oxo-ligand acting as a mere spectator. This is characteristic for low-valent states of early transition metals which have particularly large oxophilicities. We note, however, that this difference is not related with the mere charge of the systems, as the osmium-monoxide cation OsO^+ also activates methane to afford the carbeno-metal-oxide $(CH_2)OsO^+$ and thus involves a redox change from formal Os^{III} to Os^{V}.[178]

The most common way of methane activation by cationic metal oxides MO^+ involves an addition of a C−H bond across the metal-oxo unit to yield the insertion species $(CH_3)M(OH)^+$, from which reductive elimination liberates methanol as the desired product of partial oxidation. The use of gas-phase models to understand this process has been reviewed repeatedly,[14,203,204] and we will return to it in the theoretical section and thus not further dwell upon it here other than the summary given in form of Table 5. Conceptually interesting is, however, that it has been argued recently that the reactivity of metal-oxide species, either as mononuclear entities or as clusters, with respect to C−H bond activation and oxygenation reactions is by and large determined by the radical character of the oxygen atoms involved.[246,247]

Table 6. Experimentally Studied Reactions of Larger Ionic Metal Complexes $[ML]^{\mp}$ with Alkanes (Denoted as Substrate), the Major Processes Observed, the Method Used, and the Year of Publication[a]

$[ML]^{\mp}$	substrate	process(es)	method	comments	year
$Sc(C_6H_4)^+$	alkanes	C−H	ICR + theory	CH_4: n.r.	1991[277]
$Ti(CH_4)_n^+$		C−H	CID	$n = 1-5$	1995[278]
$Cr(C_6H_4)^+$	alkanes	C−H, C−C	ICR	CH_4: slow	1992[279]
$Fe(C_6H_4)^+$	alkanes	C−H, C−C	ICR		1990[280]
$Co(CH_4)_n^+$		C−H	CID		2001[281]
$CpCoO^-$	alkanes		flow tube	n.r.	1987[282]
$(phen)CuO^+$	C_3H_8	C−H	GIB + theory	labeling	2004[283]
$CpRhH^+$	cyclopentane	C−H	ICR	photoinduced	1989[284]
$LPtCH_3^+$	CID, C_6H_6	C−H	GIB		2005[285]
$LPtCH_3^+$	CH_4	C−H	GIB	H/D exchange	2007[275]

[a] For the definition of abbreviations, see footnotes of Table 3.

Before closing this subsection, we would like to highlight the heuristic aspect in the reactions of transition-metal oxides. Thus, the “four-atom reaction” of $FeO^+ + H_2$ leading to the trivial products, $Fe^+ + H_2O$, led to the concept of two-state reactivity (TSR),[248] to which we return in the next section and which has a separate account in this issue of *Chemical Reviews*. Developed for the explanation of genuine mass spectrometric data, the TSR concept has found wide uses in various areas of chemistry with implications for physics, biology, and medicine.

4.4. Miscellaneous Metal Complexes

By and large, due to the development of electrospray ionization, also a few more complex organometallic compounds became amenable for gas-phase studies. It goes without saying, however, that the number of alkane-activating species among these more complex, necessarily better coordinated metal ions, relative to the total number of species investigated, is much lower. A few cases are known, however (Table 6), among which the methane-cluster-mediated bond activation, e.g. $M(CH_4)_n^+ \rightarrow M(CH_3)_2(CH_4)_{n-2}^+$,[273] and the rich chemistry of gaseous Pt^{II} complexes are particularly insightful;[274] in the latter, methane activation can occur as a quasi-degenerate exchange of Pt-bound methyl ligands by CD_3 from deuterated methane, i.e. $LPtCH_3^+ + CD_4 \rightarrow LPtCD_3^+ + CH_3D$.[275,276]

5. Alkane Activation by Transition-Metal Ions: Theoretical Work

This section gives a summary of theoretical work, which has been done in order to understand the chemical behavior of small metal fragments, either ionic or neutral, with respect to their reactivities with hydrocarbons. In this context, a large body of studies about the electronic structures of catalysts has been performed. Later, with further developments in both soft- and hardware, the reaction mechanisms were explained based on calculations of the potential-energy surfaces (PES). Nowadays, theoretical studies are an almost implicit part of gas-phase studies, primarily due to the large expansion of density functional theory (DFT) methods in the last two decades. This phenomenon is described in a separate subsection about the “*invasion*” of DFT methods. A dominant reactivity feature of many transition-metal compounds is their ability to (i) undergo a series of simple redox transitions and (ii) rapidly allow for intersystem crossing processes. The facile spin flips between high- and low-spin states in terms of two-state reactivity often enable an activation of covalent C−H and C−C bonds, which form the topic of this review. The general reactivity patterns observed so far and the principles of the TSR pattern are described in a further subsection. The next subsection provides an overview of theoretical work concerning the activation of alkanes with bare metal cations, and we also address work concerning bond activation by metal atoms and anions. The focus is dedicated to the work of Holthausen et al. on the reaction mechanism of the C−H and C−C bond activation in the reaction of Fe^+ with ethane. In a subsection about the reactions of metal-oxide cations with methane, the focus is given to the main mechanisms operating in the reactions of bare metal oxides and to the differences observed for ligated metal oxides. The section is concluded by an account about catalytically active sites and the choice of appropriate gas-phase models for the investigation of catalytic processes observed in the condensed phase. It is shown that theoretical modeling can rely on a broad variety of approaches and can provide appropriate answers to the questions posed by condensed-phase catalysis.

5.1. Invasion of DFT Methods

The appropriate quantum chemical description of transition-metal compounds requires a proper inclusion of electron-correlation effects. Due to the substantial computational demand of such calculations, the theoretical investigations of transition-metal reactions were largely limited until about 1990. In the early years, the reactions were either described by semiempirical methods[286,287] or the approaches represented a compromise between the level of theory and the basis set used. As an example, we refer to a hybrid method of combining CCSD calculations with very small basis sets (3-21G*), with subsequent correction on the basis set obtained at the MP2 level. Such an approach was used for the description of complexes between Ag^+ and various ligands.[288] Multireference calculations were used for the description of complexes between nickel and methane or ethane already in 1983,[138b] but clearly such calculations were very expensive and therefore were not commonly applied to explain the reactivity of transition metals.

The breakthrough came in the early 1990s with spreading of the DFT methods, which are much more feasible than the post-Hartree−Fock methods, and their computational cost is about the same as for the Hartree−Fock calculations. Systematic studies of the C−H bond activation of methane by transition metals of the first and third row in 1997 demonstrated that DFT methods, namely the B3LYP hybrid functional, provide reliable results and can be applied for the investigation of the reaction mechanisms.[192] Thus, although high-level *ab initio* methods provide often more accurate results, they can also show a complete failure in

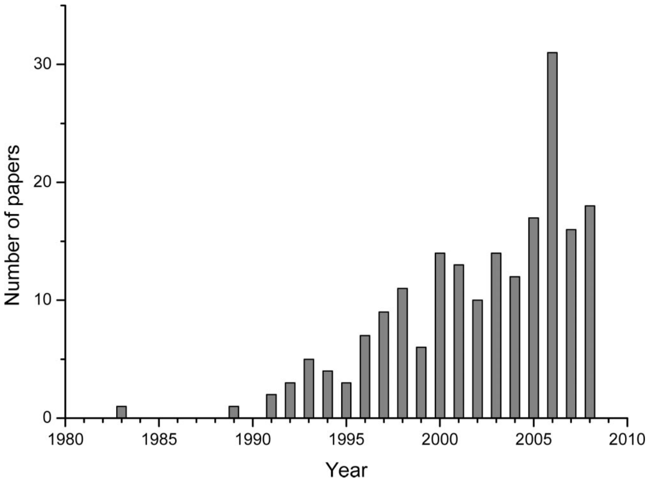


Figure 6. Number of publications with quantum chemical calculations concerning C−H and C−C bond activations occurring in the gas phase (determined from the publications cited in this review).

the description of some systems, where DFT methods still provide reasonable descriptions. In the same year, it has also been shown that iron-containing compounds can be reliably described using a combination of the B3LYP method and electron−core pseudopotentials.[289] The results obtained were in good agreement with the results obtained from higher level theoretical methods and with experiment.

The growing number of reports on the reliability of the DFT methods opened the way for the detailed description of many reactions involving transition metals and allowed theoretical descriptions of systems as large as cytochrome P450. The impressive growth of the number of theoretical papers, which is still ongoing (Figure 6), is thus not only due to the development of computer hardware but also and in the first place due to the successful application of the DFT methods.

5.2. Transition Metals: Spin Forbidden Reactions Are Not Forbidden

In the classical concept of chemical reactivity, the "well behaved" reactions proceed on a single-state potential energy surface and hopping among different spin PESs is forbidden. Such a simplistic scheme is not at all valid for reactions of transition metals. In fact, the reactions of transition metals often profit from intersystem crossings, and due to this particular mode, many reactions are conceivable, which would otherwise hardly be possible. The spin-forbidden reactions are common mainly for the first-row transition metals, because of the large exchange constants between the 3d-orbitals, which leads to a large spin−orbit coupling. The 3d orbitals are moreover rather compact, rendering the overlap with the orbitals of the ligands the smallest from all transition metals.

The theoretical assessment of the probability of the intersystem crossing is based on the calculation of spin−orbit coupling (SOC) constants. Thus, the investigation of multispin reactivity is based on the determination of SOCs for potential-energy surfaces of all spin states involved in the reaction, which leads to the localization of transition seams.[290] Such an approach requires many multireference calculations and is extremely computationally demanding.

A substantial simplification is based on the localization of minimum energy crossing points (MECPs) between the spin surfaces involved and consequently calculation of SOCs only at these points.[291−293] This concept consists in finding a common intermediate structure on the low- and high-spin surfaces with the minimum possible energy. Such a structure then represents a transition structure for a spin-flip, and the probability of the spin-flip can be estimated by the calculation of SOC. Provided that the spin−orbit coupling is large enough, the MECP appears as a regular energy barrier in a reaction, which can be lower than a barrier on a single-state PES, and such a reaction can be termed as a spin-accelerated reaction.[294] It has to be kept in mind, however, that in systems with a small spin−orbit coupling, the MECP may still represent a large kinetic barrier and the intersystem crossing should not be taken for granted. The computation of MECPs can be performed using DFT methods and therefore can be relatively easily applied even for larger systems.[295,296]

As an example of two-state reactivity (or a spin-accelerated process), we refer to the reactions of FeH^+, CoH^+, and NiH^+ with methane.[217] It has been shown experimentally that the reaction of NiH^+ with methane proceeds at room temperature, whereas the metal hydrides FeH^+ and CoH^+ do not activate methane under these conditions.[218] B3LYP calculations revealed that these reactions are typical examples of spin-accelerated reactions, where the barrier on the potential-energy surface of the ground state, i.e. high-spin state, is prohibitorily large, but if the intersystem crossing to the excited potential-energy is involved, the energy barrier is significantly reduced. In the case of the reaction of NiH^+, the minimum energy crossing points lie even below the energy of the reactants, and therefore, this reaction can be observed in the gas phase without any additional energy activation (Figure 7).

The heavier congeners of NiH^+, PdH^+, and PtH^+ [206a,236] show qualitatively the same reactivity toward methane in the experiment, but the potential-energy surfaces are completely different. The reaction of PdH^+ with methane proceeds on the singlet state PES, which is in this case the ground state PES, and the excited triplet state PES is much higher in energy; therefore, no intersystem crossings are involved in this case. On the other hand, for the $PtH^+ + CH_4$ system, the ground and excited potential-energy surfaces are very close in energy and very facile spin flips are predicted; therefore, in the context of this reaction, we may speak about multistate reactivity.[248d]

The next example concerns the reaction of FeO^+ with H_2 leading to Fe^+ and H_2O. This reaction represented a long-lasting challenge for theoreticians. The experiments showed that there are two distinct channels leading to the products Fe^+ and H_2O. The first channel leads over a barrier of about 0.6 eV and represents the dominant reaction mechanism. The minor channel corresponds to a barrier-less process and can be observed only at small collision energies.[262,297] The first theoretical studies were based on *ab initio* methods (CASPT2, CCSD(T))[298,299] and revealed that the ground state potential-energy surface corresponds to the sextet state, and the energy barrier for the reaction amounts to 0.55 eV, which perfectly explained the dominant channel observed. However, no explanation was found for the minor channel. Consideration of the excited potential-energy surface (quartet state) led to an identification of a process with an energy barrier of about 0.3 eV, which therefore could not have accounted for the observed barrierless process.

Later, the reaction was investigated with DFT methods. At this level of theory, the transition structures at the excited

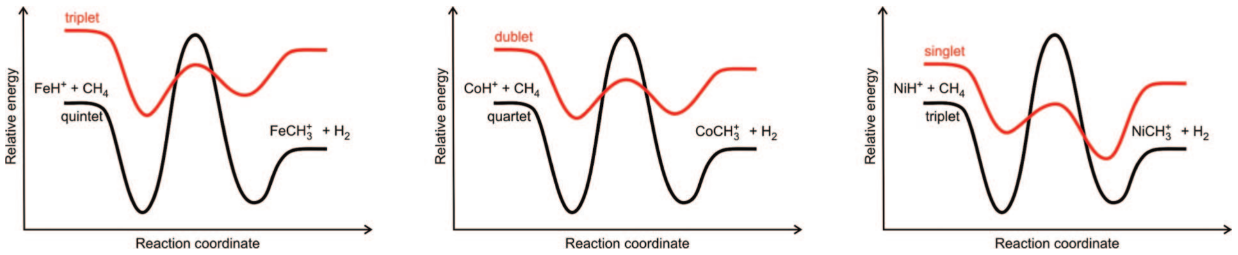


Figure 7. Schematic drawing of two-state reactivity in the systems $MH^+ + CH_4$, for M = Fe, Co, and Ni.[217]

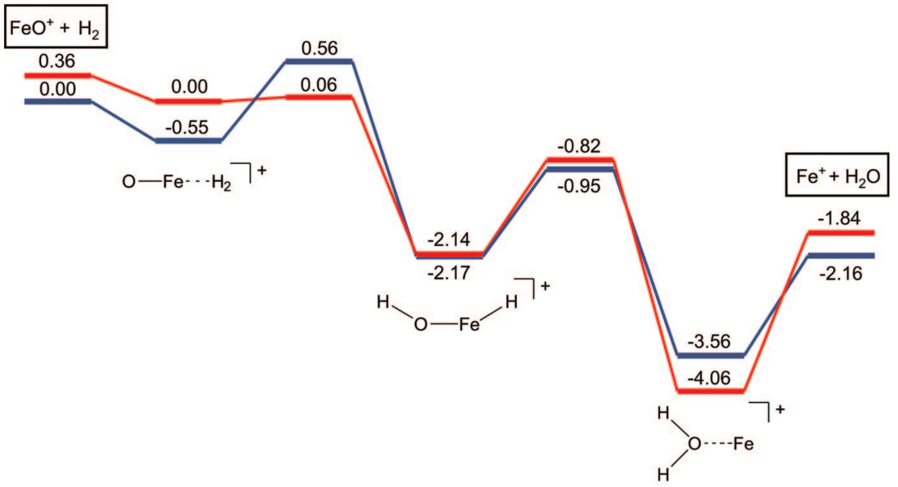


Figure 8. DMC//B3LYP potential-energy surface following the $Fe^+ + H_2O \rightarrow FeO^+ + H_2$ reaction path in the sextet (blue) and quartet (red) states. Energies are given in electronvolts and are relative to the ground-state reactants, FeO^+ ($^6\Sigma$) + H_2O.[301]

PES lie only 0.05 eV above the reactants' asymptote, and therefore, the intersystem crossing to this PES could account for the barrierless process. However, this method predicts incorrectly the relative stability of the ground and excited states of the Fe^+ product and the excited quartet state of Fe^+ appears as the ground state. Consequently, this finding questions also the energetics calculated by DFT for this system. The (so far) definite answer was given by applying the diffusion quantum Monte Carlo method,[300] which correctly predicts the spin states of all species involved and confirms that the transition structure on the excited PES lies about 0.06 eV above the reactants' asymptote (Figure 8), and therefore, the intersystem crossing explains the barrierless process observed experimentally.[301]

In the context of the reaction between FeO^+ and H_2, it should also be emphasized that not only the potential energy of MECP between the PESs is important but also the SOC has to be taken into account to correctly predict the reactivity. Hence, as soon as the collision energy of the reactants is sufficient to surmount the energy barrier on the sextet PES, the reactivity is dominated by the process with the larger energy barrier, because the channel leading via the spin flip is kinetically hindered. Thus, neglect of the important role of SOC may lead to a misinterpretation of the obtained results.

In general, we can say that the large advantage of transition metals with respect to their involvement in the activation of covalent bonds lies in the accessibility of several spin states, which can be differently stable along the pathways of a "radical cleavage" of a covalent bond. The unique electronic structure of transition metals thus allows for spin-flipping along the reaction pathway such that the most favored combination of thermodynamic and kinetic control can be achieved.

5.3. Reactions of Metal Cations with Alkanes

One of the simplest models for the competition of C−H and C−C bond activation is a reaction between ethane and a bare metal ion. A nice story of how computations can shed light on reaction mechanisms is the investigation of elementary steps in the reaction of the iron cation with ethane. It is known from the experiment that the thermal interaction between Fe^+ and C_2H_6 leads only to the formation of an adduct. At elevated collision energies, the dissociation of the adducts back to the reactants was observed along with minor expulsions of methyl or ethyl radicals.[115,198a,b,302] Formation of thermodynamically favored products, i.e. $FeC_2H_4^+$ and $FeCH_2^+$, which could be expected based on analogy with reactions of higher alkanes,[1b] was not observed at all. It has been concluded that these reactions are hindered by energy barriers. The direct C−C bond activation was predicted to be associated with a sizable barrier, which would prohibit this channel.[117] For the C−H bond activation, it was expected that the initially formed insertion complex $[H{-}Fe{-}CH_2{-}CH_3]^+$ undergoes a β-hydrogen transfer to iron to form a dihydrido complex $[(H)_2Fe{-}C_2H_4]^+$, which finally, in the rate determining step, releases a H_2 molecule by a reductive elimination mechanism.

Employment of the B3LYP method by Holthausen et al. completely turned this picture over. First, it has been shown that the C−C bond activation proceeds via an energy barrier lying below the energy asymptote of the reactants.[303] This suggested, contrary to the predictions based on experiments, that already the thermal collisions of reactants lead to the $[CH_3{-}Fe{-}CH_3]^+$ intermediate. The next transition structure representing a concerted rearrangement of a hydrogen atom from one to the other methyl group is the one which is prohibitively high in energy and hinders the elimination of

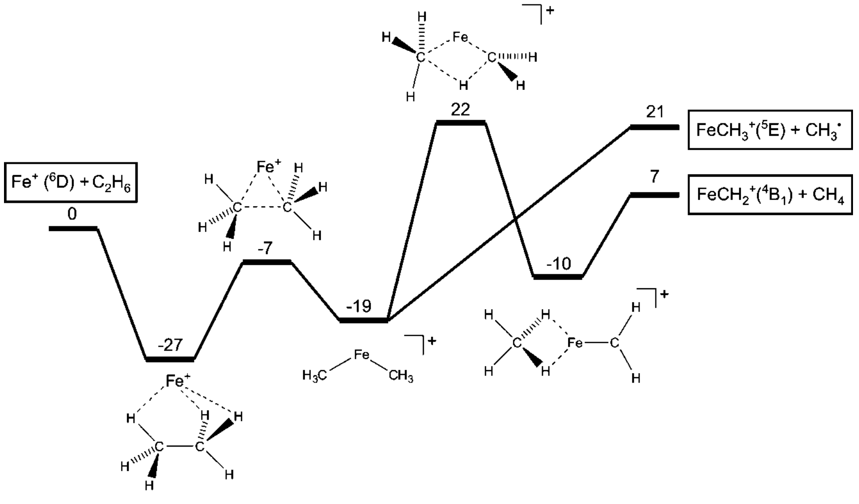


Figure 9. C−C bond activation in the reaction $Fe^+ + C_2H_6$ investigated at the B3LYP level of theory. Energies are given in kcal/mol.[304]

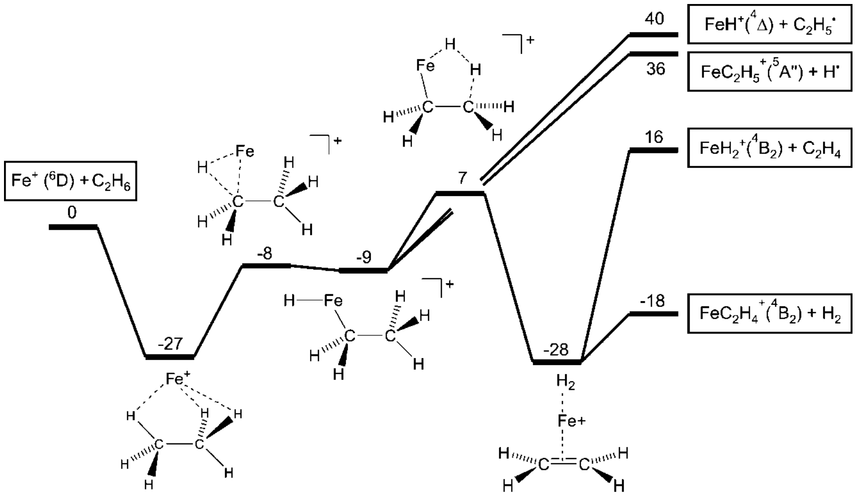
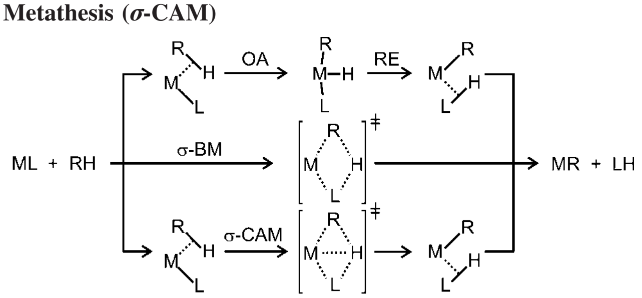


Figure 10. C−H bond activation in the reaction $Fe^+ + C_2H_6$ investigated at the B3LYP level of theory. Energies are given in kcal/mol.[304]

Scheme 12. Mechanistic Variants for Transition-Metal Mediated C−H Bond Activation of Hydrocarbons RH: Oxidative Addition−Reductive Elimination (OA-RE), σ-Bond Metathesis (σ-BM), and σ-Complex Assisted Metathesis (σ-CAM)



methane (Figure 9).[304] The reaction pathway for the C−H bond activation has a similar topology (Figure 10). The initial insertion of an iron cation to the C−H bond proceeds via an energy barrier lying below the energy of the reactants. In the second step, the β-hydrogen is transferred so that directly a complex of the iron cation with ethylene and a hydrogen molecule is formed. This rearrangement proceeds via a kinetic barrier above the energy of the separated reactants and explains why the dehydrogenation product is not observed experimentally. Any involvement of the experimentally predicted dihydrido complex was excluded.

The B3LYP study of the Fe^+/C_2H_6 system explained all experimental data and helped to establish the overall understanding of the elementary steps in the C−H and C−C bond activations of alkanes by bare metals and metal ions. For example, the application of an analogous method to the reactions of Fe^+, Co^+, and Ni^+ with propane revealed that the reaction proceeds first via a bond-insertion of the metal into a C−H or C−C bond of the alkane. In the second step, molecules of H_2 or CH_4, respectively, are eliminated via multicentered transition structures. The latter represent the largest barriers along the reaction pathways and therefore determine the reactivity of the metals. The reaction mechanisms are fully analogous to the Fe^+/C_2H_6 system (Figures 9 and 10). The relative energies of the reactants, intermediates, energy barriers, and products indeed depend on the nature of reactants. Thus, in reactions of Fe^+ and Ni^+ with propane, preferential losses of methane are observed, whereas the reaction of Co^+ and propane leads preferentially to dehydrogenation.[130b]

Another important consequence of the theoretical study of the Fe^+/C_2H_6 system is the introduction of a concerted pathway, in which a hydrogen atom (or an alkyl group) from one ligand is directly transferred to another ligand bound to the central metal. This reactivity mode challenges the classical “oxidative addition−reductive elimination” reactiv-

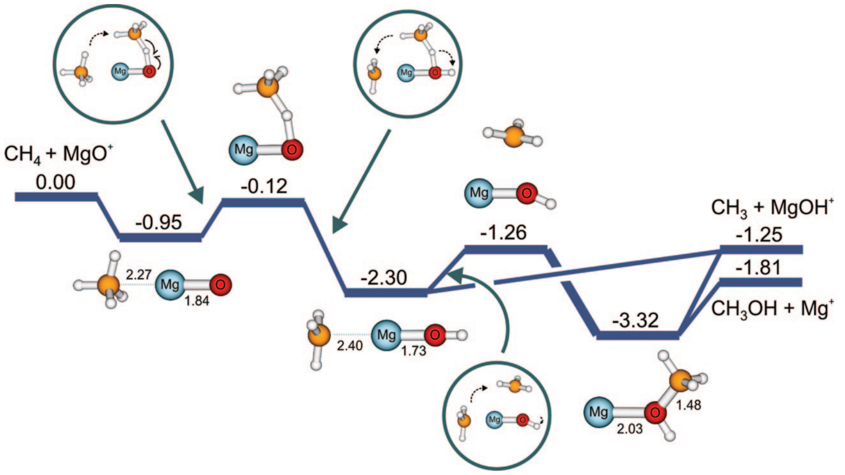


Figure 11. Potential-energy surface (in eV) for the reaction of MgO^+ with CH_4 calculated at the MP2/6-311+G(2d,2p) level of theory; selected bond lengths are given in angstroms. The encircled structures depict the rearrangements occurring along the reaction coordinate.[58a]

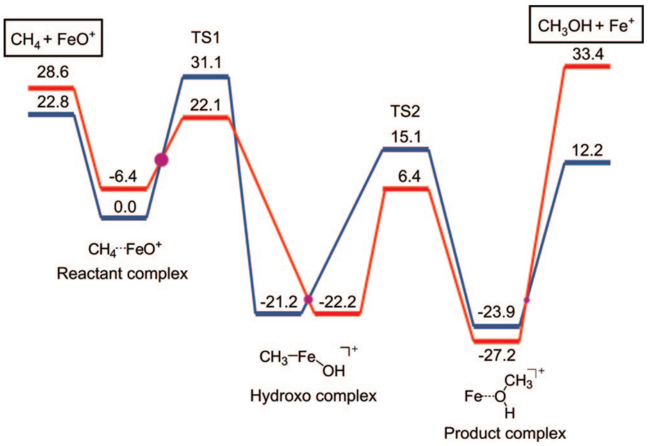


Figure 12. Potential-energy surface (in kcal/mol) for the reaction of FeO^+ with CH_4 in the quartet (red) and sextet (blue) states calculated at the B3LYP level of theory. The closed violet circles indicate crossing seams.[290]

ity picture (see Scheme 6 in section 4), which assumes the involvement of the dihydrido-complex $(H)_2Fe(C_2H_4)^+$. The analogous reactivity picture in reactions of ML (M is a neutral or charged transition metal and L is a ligand) with alkanes led to an establishment of an alternative mechanistic scenario termed σ-complex-assisted metathesis (σ-CAM, Scheme 12). This reaction mechanism first involves formation of a complex between the reactants. In the second step, a hydrogen atom or an alkyl group from the coordinated alkane is directly transferred to the ligand L to form a complex of products.

The competition between "oxidative addition–reductive elimination" (OA/RE) and σ-complex-assisted metathesis (σ-CAM) has been systematically investigated by the degenerate ligand exchange reaction for MCH_3^+ (M = Fe–Ni, Ru–Pd, and Os–Pt) with CH_4.[205] It has been shown that the 3d metals favor the mechanism of σ-CAM. However, the transition structure for the concerted rearrangement often represents a high energy barrier, as also found in the system Fe^+/C_2H_6. The degenerate ligand exchange in the model system with 3d metals could have been thus observed only for the $NiCH_3^+/CH_4$ system. The 4d and 5d transition metals prefer the classical reaction pathway via the OA/RE mechanism; only in the case of the Pd complex are both mechanisms energetically very similar. As observed also in other systems, the reactivities of 4d and 5d metals differ with respect to the involvement of an intersystem crossing. Thus, whereas the reactions of the 4d metals take place on the ground potential-energy surfaces, the involvement of efficient spin flips is typical for the 5d metals. The theoretical studies on alkane activation are briefly summarized in Table 7.

5.4. Reactions of Metal-Oxide Cations with Methane

The oxidation of methane to methanol is most often modeled by a simple reaction between neutral or charged metal oxide $MO^{-/0/+}$ and methane. This reaction has been studied for an impressive number of the main-group and transition-metal oxides (Table 8). In fact, three major mechanistic scenarios have been proposed. The first one involves formation of a $CH_3-M-OH^{-/0/+}$ intermediate, which consequently undergoes a rearrangement to the complex of metal and methanol. The second leading mechanism is analogous to the former but involves an intersystem crossing along the reaction pathway. The last mechanism supposes the abstraction of a hydrogen atom from methane by a metal oxide to form a pair of $MOH^{-/0/+}$ and a methyl radical. In the subsequent step, the methyl radical "rebounds" to the oxygen atom, which leads to the complex of methanol and the metal.[353] The following paragraphs show some selected examples for these scenarios.

The simplest reaction mechanisms for these processes can be found in mechanistic studies of the C–H activation by radical cations of oxides derived from the main-group metals. The mechanism is demonstrated for the reaction of MgO^+ with methane (Figure 11).[58a] The reaction starts with a formation of an encounter complex between the reactants, in which the metal atom interacts with the carbon atom of methane in the axis of the Mg–O bond. In the following step, the methane molecule "walks" around the magnesium atom toward the oxygen atom, which bears an unpaired electron, to finally transfer one hydrogen atom and form a $CH_3-Mg-OH^+$ intermediate. The optimized geometry of the intermediate has again a linear arrangement of the carbon, magnesium, and oxygen atoms. Formally, this intermediate represents a complex between protonated magnesium oxide and a methyl radical. Consequently, it can directly lose the methyl radical, which is also observed experimentally. The final rearrangement to methanol starts again by "walking" of the methyl group around the metal atom toward the oxygen atom, but this time the entire methyl group is

Table 7. Theoretically Studied Reactions of Anionic, Neutral, or Mono- or Dicationic Bare Metal Atoms $[M]^{-/0/N+}$ with Alkanes (Denoted as Substrate), the Major Products Investigated, the Method Used, the Year of Publication, and a Note Whether Single-State, Two-State, or Multistate Reactivity Has Been Investigated

$[M_m]^{-/0/n+}$	substrate	product(s)	level of theory	year	SSR/TSR/ MSR
Be^+	c-C_3H_6	propylene ethylene	QCISD(T)/6-3lG*//HF/6-31G*	1992[305]	SSR
Be, Mg, Ca Pd, Zn, Cd	CH_4, CH_3Cl	C−H, C−C insertions	BLYP/TZ(2)P-STO relativistic effects ZORA	2006[306]	SSR
Sc^+	CH_4	CH_2, $ScCH_2^+$	MR CASSCF MR-SDCI-CASSCF	1996[307]	SSR
Sc^+	CH_4 (NH_3, H_2O)	CH_2, $ScCH_2^+$	B3LYP/DZVP:TZVP	2001[308]	SSR
Sc^+	CH_4, C_2H_6, C_3H_8	CH_2, C_2H_4, C_2H_2, CH_4, CH_4, C_2H_4, C_2H_6, C_3H_6	B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G**	2003[309]	
Sc^+	CH_3OH	CH_3ScOH, CH_3OScH	B3LYP/6-311++G**	2004[250]	SSR
Sc^+	$HCCCH_2OH$	$ScC_3H_2^+$, $C_3H_3O^+$	MP4/LanL2DZ:6-311+G**//B3LYP/DZVP	2008[310]	
Sc^+	2-methylcyclohexanol	CH_3ScOH^+, $HScOH^+$	B3LYP/6-31G**//B3LYP/3-21G**	2003[311]	
M^+ (M = Sc−Cu)	CH_4	inversion	B3LYP/Wachters:6-311G**	1999[312]	SSR
M^+ (M = Sc−Cu)	CH_4	inversion	B3LYP/Wachters:6-311G**	2001[313]	SSR
M^+ (M = Sc−Cu)	$HMCH_3^+$	insertion	CASPT2/ANO	1997[314]	
M (M = Sc−Ni; La−Pt)	CH_4	CH_3−M−H	B3LYP/LANL2DZ CCSD MCPF	1997[192]	
Ti^+	C_2H_6	$TiC_2H_4^+$, $TiCH_2^+$	B3LYP/TZVP CCSD(T)/6-311+G(2d,2p) MCQDPT2/ TZV+f	2000[92]	TSR
Ti^+	C_2H_6	$TiC_2H_4^+$, $TiCH_2^+$	B3LYP/6-311++G(3df,3pd)// B3LYP/6-311+G(d,p)	2005[315]	
Ti^+	C_3H_8	$TiC_3H_6^+$, $TiC_2H_4^+$	B3LYP/Wachters:6-311+G(2d,2p)	2008[316]	TSR
Ti^+	N_2O	$TiO^+ + N_2$	B3LYP	2006[317]	TSR
Ti^+, V^+, Cr^+	CH_4, NH_3	MCH_2^+, MCH_3^+, MH^+, analogous for NH_3	B3LYP/DZVP:TZVP	2002[252a]	TSR
V^+, VO^+	CH_3OH		DFT	2005[251b]	
M^+, MO^+ (M = V, Nb, Ta)	CH_3OH	CH_4	B3LYP/LANL2DZ:6-31G*	2004[251a]	TSR
Cr^+	CH_3CHO	CH_4	UB3LYP/6-311+G(2df,2pd)	2006[318]	SSR
Mn^+	CH_4 (H_2O, NH_3)	$MnCH_2^+$, $MnCH_3^+$, MnH^+	B3LYP/DZVP:TZVP	2003[110c]	SSR
Mn^+	CH_4, NH_3	$MnCH_2^+$	B3LYP/DZVP:TZVP	2002[110b]	TSR
$Fe^{-/0/+}$	CH_4	$Fe(CH_4)^{-/0/+}$, $HFeCH_3^{-/0/+}$	MINDO/SR	1992[319]	
Fe	CH_4, C_2H_6, C_3H_8	adducts	CASPT2/ANO	1997[320]	
Fe^+	CH_4 (H_2O, NH_3)	$FeCH_2^+$, $FeCH_3^+$, FeH^+	B3LYP/DZVP:TZVP	2004[321]	SSR, TSR
Fe_2^+	CH_4	Fe_2H^+ $Fe_2CH_2^+$ $Fe_2CH_3^+$	B3LYP/DZVP BPW91/DZVP	2006[322]	TSR
Al_4Fe	CH_4, C_2H_6, C_3H_8, C_3H_6	C−H activation	B3LYP/LANL2DZ:6-311++G**	2007[323]	SSR
Fe^+	CH_3CHO	CH_4	UB3LYP/6-311+G(2df,2pd)	2006[318]	TSR
Fe^+	C_2H_6	$FeC_2H_4^+$, $FeCH_2^+$	B3LYP/Wachters:D95**	1996[304]	SSR
Fe^+	C_2H_6	$FeC_2H_4^+$, $FeCH_2^+$	B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(d,p)	2003[324]	SSR
M = Fe−Ni, Rh, Pd	C_2H_6	CH_3−M−CH_3, C_2H_5−M−H	CCI	1991[325]	SSR
Fe^+	C_3H_8	$FeC_3H_6^+$, $FeC_2H_4^+$	B3LYP/D95**	1996[303]	TSR
Fe^+−Ni^+	C_3H_8	$MC_3H_6^+$ $MC_2H_4^+$	B3LYP/6-311++G(2d,2p)	2000[130b]	SSR
Fe^+	$C_2H_5SiH_3$	CH_4, H_2, C_2H_4, SiH_4	B3LYP/VDZ	2000[326]	SSR
Fe^+	n-C_3H_7OH	i-C_3H_7OH	mPW1PW91/TZV:6-31+G*	2003[20d]	
Fe^+	N_2O	$FeO^+ + N_2$	B3LYP/6-311+G*	2005[41i]	SSR
M^+ (M = Fe, Co)	$C_8H_{17}CN$	$MC_8H_{15}CN^+$	BLYP/ECP:DZVP	1997[327]	SSR
M^+ (M = Fe, Co)	CF_3	$MF^+ + CF_2$	B3LYP/HW:6-311+G*	1998[227]	SSR
Co^+	CH_4	$CoCH_2^+$, $CoCH_3^+$, CoH^+	CASSCF, MR-SDCI-CASSCF	1993[328]	SSR
Co^+	RH (R= CH_3, C_2H_5, C_3H_7)	$HCoR^+$	CASSCF	1996[329]	SSR/TSR
Co^+	C_2H_6	$CoCH_2^+$, $CoCH_3^+$, CoH_2^+, $CoC_2H_4^+$	B3LYP/WachtersH:D95**//B3LYP/HW:D95**	1996[330]	SSR
Co^+	C_3H_8	$CoC_2H_4^+$, $CoC_3H_6^+$	MRMP2//CASSCF/SBK*	2000[331]	SSR
Co^+	$C_2H_5SiH_3$	CH_4, H_2, C_2H_4, SiH_4	B3LYP/VDZ, B3LYP/VTZ	2000[332]	SSR
Co^+	CH_3CHO	$CH_4 + CO$	B3LYP/6-311+G(2df,2pd)	2005[333]	SSR
Ni^+	CH_4	$NiCH_2^+$	B3LYP/SDD:6-31G**	2001[334]	SSR
Ni^+	CH_4	$NiCH_2^+$, $NiCH_3^+$, NiH^+	B3LYP/ 6-311++G(3df,3p)//B3LYP/6-311+G*	2005[34b]	SSR
Ni	CH_4, C_2H_6	$Ni(H)(CH_3)$, $Ni(CH_3)_2$	CI/DZ	1983[138b]	SSR
Ni	C_2H_4	C−H, C−C	B3LYP/6-311++G(d,p)	2007[335]	SSR
Ni^+	C_2H_6	$NiC_2H_4^+$, $NiCH_2^+$	B3LYP, BLYP	2002[139b]	
Ni^+	C_3H_8	$NiC_3H_6^+$, $NiC_2H_4^+$	B3LYP/6-311+G(2d,2p)//B3LYP/LANL2DZ, RRKM	1998[140b]	SSR
Ni^+	C_3H_8	$NiC_3H_6^+$	B3LYP/6-311++G(3df,3pd)	2002[336]	
Ni^+	C_2H_5−XH_3, C_2H_3−XH_3 (X = C, Si, Ge)	adducts	B3LYP/6-311+G(2df,2p)//B3LYP/6-311G(d,p)	2003[337]	SSR
Ni^+	CH_3COCH_3	$C_2H_6 + CO$	B3LYP/6-311+G(2df,2pd)	2006[338]	SSR
Ni^+	CH_3CHO	CH_4	B3LYP/6-311+G(2df,2pd)	2007[339]	
Ni^+	C_4H_{10}	$Ni(C_4H_8)^+$, $Ni(C_3H_6)^+$, $Ni(C_2H_4)^+$	B3LYP/6-311+G(2d,2p//B3LYP /LANL2DZ, RRKM	1999[70]	SSR

Table 7. Continued

$[M_m]^{-/0/n+}$	substrate	product(s)	level of theory	year	SSR/TSR/MSR
Cu^+	$(CH_3)_2CHOH$	C_3H_6, $(CH_3)_2CO$	B3LYP/6-311++G(d,p)	2002[340]	SSR
M^+ (M = Na, Cu)	CH_4	$M(CH_4)^+$	SCF	1993[341]	
Zr^+	CH_4	$ZrCH_2^+$, $ZrCH_3^+$, ZrH^+	B3LYP/HW+:6-311++G(3df,3p)	2003[34c]	SSR
Zr^+	HF, HCl, H_2O, H_2S, NH_3, PH_3, CH_4, SiH_4	insertion to the H−X bond	B3LYP/LANL2DZ:6-31G**, MP2/LANL2DZ:6-31G**, SP at higher levels of theory	2003[149]	SSR
M^+ (M = Y−Tc, Rh)	CH_4	$CH_3{-}M{-}H^+$	MCPF//HF/HW:DZ	1994[342]	TSR
Nb^+	C_2H_6	$NbC_2H_4^+$, $NbCH_2^+$	B3LYP/LANL2DZ:6-311+G(2df,2p)	2008[65]	TSR
M = Nb, Rh	CH_4	$CH_3{-}M{-}H$	MCPF	1991[343]	SSR/TSR
Mo^+	CH_4	$MoCH_2^+$, $MoCH_3^+$, MoH^+	B3LYP/HW:6-311++G(3df,3p)	2006[34e]	TSR
Mo	CH_4	$HMoCH_3$	B3LYP/SDD:6-311++G (3df, 3pd)	2008[344]	MSR
Mo^+	C_2H_6, C_3H_8	C−H, C−C	B3LYP/HW:6-311++G(3df,3p)	2007[156]	TSR
Rh^+	CH_4	$RhCH_2^+$	CASSCF, MR-SDCI-CASSCF	1993[328]	SSR
Rh^+	CH_4	$RhCH_2^+$	B3LYP/HW:DZ, PCI-80/Huzinaga	1998[162b]	TSR
Pd	CH_4	$CH_3{-}Pd{-}H$	reaction path Hamiltonian (RPH) approximation based on LCAO, MO, CNDO/S2	1995[345]	
Pd	CH_4, C_2H_6, CH_3Cl	$CH_3{-}Pd{-}H$, $CH_3{-}Pd{-}CH_3$, $CH_3{-}Pd{-}Cl$	BP86/TZ(2)P-STO, relativistic effects ZORA	2001[346]	SSR
Pd	XH_4 (X = C, Si, Ge, Sn, Pb)	$H{-}Pd{-}XH_3$, $H_2{-}Pd{-}XH_2$	ZORA-BLYP/TZ2P	2006[347]	
Pd, Pd_2, Pd_3, Pt, Pt_2, Pt_3	H_2, CH_4	H−H, C−H	B3LYP/HW:DZ, single points with larger BS	1998[182d]	SSR, TSR
Ag^+	L (L = H_2O, NH_3, C_2H_4, C_2H_2, etc.)	AgL^+	MP2/RECP:3-21G*	1998[288]	SSR
M = La−Lu, Th	CH_4	CH_3MH	B3LYP/LC-ECP:6-311G(2df,2pd)	2006[348]	
Hf^+	CH_4	$HfCH_2^+$	B3LYP/HW+:6-311+G(3df,3p)	2006[34g]	SSR
Ta^+	CH_4	$TaCH_2^+$	B3LYP/HW:D95	1997[172b]	TSR
Ta^+	$CH_4 + CO_2$	CH_2CO	B3LYP/RECP:D95	1998[172c]	TSR
Ta^+	CH_4	$TaCH_2^+$, $TaCH_3^+$, TaH^+	B3LYP/HW+:6-311++G(3df,3p), BHLYP/HW+:6-311++G(3df,3p)	2007[34h]	SSR
W^+	CH_4	WCH_2^+, WCH_3^+, WH^+	B3LYP/HW+:6-311++G(3df,3p)	2006[34i]	MSR
Re	CH_4	$HCReH_3$	PW91/TZ2P	2009[349]	MSR
Re^+	CH_4	$ReCH_2^+$	B3LYP/HW+:6-311++G(3df,3p)	2004[34j]	MSR
Os^+	CH_4	$OsCH_2^+$	B3LYP/LANL2DZ:6-311G**	2003[178]	MSR
Ir^+	CH_4	$IrCH_2^+$	MCPF//HF/RECP:Huzinaga	1994[180]	TSR
Ir^+	CH_4	$IrCH_2^+$	B3LYP/HW+:6-311+G(3df,3p)	2006[34k]	MSR
Ir_2	H_2	Ir_2H_2	CI/TZ//HF/RECP	1998[350]	
Pt^+	CH_4	$PtCH_2^+$	B3LYP/RECP:DZ	1995[5d]	
Pt	CH_4	$PtCH_2^+$	PCl-80	1995[182c]	SSR
Pt^+, PtO^+	CH_4	$PtCH_2^+$, CH_3OH	B3LYP/6-311+G(3d,2p)//B3LYP/HW:DZ, PCI-80/Huzinaga	1997[5e]	SSR
Pt^+	CH_4	$PtCH_2^+$	B3LYP/6-311G**//B3LYP/6-31G*	1998[3a]	SSR
Pt^+	CH_4	$PtCH_2^+$, $PtCH_3^+$, PtH+	B3LYP/HW+:6-311++G(3df,3p)	2001[5g]	SSR
Pt^+	$CH_4 + NH_3$	CH_2NH	B3LYP/RECP:TZP//RECP:DZP	1999[3c]	SSR
Pt^+	N_2O	$PtO^+ + N_2$	UB3LYP/RECP:6-311+G(2d), MECP	2005[41i]	TSR
PtM^+, M = Cu, Ag, Au; Pt_n^+ ($n = 2 - 4$)	CH_4	$PtMCH_2^+$	BPW91/TZ(2)P-STO relativistic effects ZORA	2006[351]	TSR
Au^+	CH_4	$AuCH_2^+$, AuH^+, $AuCH_3^+$	B3LYP/HW+:6-311++G(3df,3p)	2006[34m]	SSR
M^+ (M = Th, U)	CH_4	MCH_2^+	PW91/ZORA, B3LYP/SDD	2009[352]	SSR

transferred to the hydroxyl group, the molecule of methanol is formed, and the radical site is transferred to the magnesium cation.

The typical example of a reaction between a transition-metal oxide cation and methane, which involves an intersystem crossing, is the reaction $FeO^+ + CH_4$ (Figure 12). The reaction is initiated by the formation of a complex, where methane is coordinated to the iron atom. The following migration of a hydrogen atom to the oxygen atom proceeds via a four-membered transition structure, as was described for MgO^+. In this case, however, the transition structure lies above the potential energy of the reactants, and therefore the occurrence of this reaction at room temperature implies involvement of an intersystem crossing. It has been shown by Yoshizawa et al. that the transition from the sextet PES to the quartet PES decreases this barrier by about one-third and makes this reaction possible to proceed.[290] The relevant spin−orbit coupling constant amounts to 133.6 cm^{-1}. The reaction then continues to the formation of a complex between the iron cation and methanol, which can be realized on the quartet potential-energy surface. A possible spin-flip to the sextet PES would result in a higher energy barrier for the rearrangement and therefore is not envisioned. Moreover, the SOC value drops almost by a factor of 10 with respect to the first crossing seam. The final release of a methanol molecule should be again associated with a transition to the sextet PES; however, the SOC is almost zero and therefore such a process is improbable.

The reactions of all 3d transition-metal oxide cations with methane start with the formation of analogous reactant complexes. The details of PESs after the formation of the initial encounter complex then strongly depend on the nature of the 3d metal.[354] However, we can find several general trends. First, the early transition-metal oxides ScO^+, TiO^+, VO^+, CrO^+, and MnO^+ have low-spin ground states. This alters the potential-energy surface so that the intersystem crossing does not occur in the vicinity of TS1 but instead in the vicinity of TS2. The ground states of the products are high spin, and thus, only one spin flip is necessary. Second, the reactions of ScO^+, TiO^+, and VO^+ with methane are

Table 8. Theoretically Studied Reactions of Anionic, Neutral, and Cationic Metal Oxides $[M_mO_n]^{-/0/+}$ with Alkanes (Denoted as Substrate), the Major Products Investigated, the Method Used, the Year of Publication, and a Note Whether Single-State, Two-State, or Multistate Reactivity Has Been Investigated[a]

MO^+/MO_n^+	substrate	product	level of theory	year	SSR/TSR/MSR
MO^+ (M = Li, Be, Mg, Al)	CH_4	CH_3OH, MCH_3^+, MOH^+	MNDO PM3	1994[286]	SSR
Li_2O	CH_4	CH_3OH, CH_3Li	B3LYP/6-311++G(3df,3pd), CCSD(T)/6-311++G(2d,2p)	2005[362]	SSR
BeO	CH_4	CH_3	G2M(MP2)//MP2/6-31g**	2001[363]	SSR
MgO^+	CH_4	CH_3	MP2/6-311+G(2d,2p)	2006[58a]	SSR
CaO	CH_4	CH_3OH	QCISD/6-311++G(3df,3pd)//B3LYP/6-311+G(2df,2p)	2006[364]	
Al_4CaO	CH_4	CH_3OH	B3LYP/6-311++G**	2006[365]	SSR
$(Al_2O_3)_x^+$	CH_4	CH_3	B3LYP/TZVP	2008[366]	SSR
MO (M = Sc, Ni, Pd)	CH_4	CH_3OH	B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p), SP at higher levels of theory	2002[367]	TSR
MO^+ (M = Sc−Zn)	structure		BLYP, B3LYP, MRMP, MR-SDCI, SA-CASSCF	2001[368]	
MO^+ (M = Sc−Cu)	CH_4	CH_3OH	B3LYP/Wachters:6-311G**	2000[354]	TSR
TiO_2, VO_2	C_2H_2	C_6H_6	B3LYP/TZVP	2008[369]	SSR
TiO	CH_4	$Ti(CH_3)_2(OH)H$	CCSD(T)/6-311++G**//B3LYP/6-311++G(3df, 3pd)	2006[244]	SSR
VO^+	CH_3OH	$[VO(CH_2O)]^+$	B3LYP/TZVP	2005[19c]	SSR
VO^+	CH_4	CH_3OH	B3LYP/cc-pVTZ, MR-CI/cc-pVQZ	2007[252b]	SSR
VO_2^+	C_2H_6, C_2H_4	C_2H_4, CH_3CHO	B3LYP/HW:6-311+G(2d,p)//B3LYP/LANL2DZ	1999[19a]	SSR
VO_2^+	C_3H_8	$C_3H_5VO(OH)^+$	B3LYP/Wachters:6-311G**	2003[19b]	TSR
VO_2^+	C_2H_6	C_2H_4	B3LYP/6-311G(2d,p)	2004[253]	TSR
VO_2^+	$CH_3{-}CCH$	various oxidation products	B3LYP/6-311G(2d,p)	2008[370]	TSR
VO_3	C_2H_4, C_2H_2	CH_2O, CH_3CHO, CH_2CHOH, H_2O, CH_2CO	B3LYP/TZVP	2008[371]	MSR
VO_3^-	CH_3OH, CH_3CH_2OH	CH_2O	B3LYP/SDD:6-311++G**	2006[372,373]	TSR
silsesquioxane ($VSi_7O_{12}H_7$), $O{=}V(OH)_3$	C_3H_8	C_3H_6	B3LYP/TZVP	2008[374]	SSR
$VO(OCH_3)_3$, $VO(OCH_3)_3^+$, $(VO(OCH_3)_3)_2$	CH_3OH	CH_2O	B3LYP/TZVP	2005[375]	
$OV[OSi(OH)_3]_3$	CH_3OH	CH_2O	B3LYP/LANL:6-31G	2002[376]	
V_2O_5 (010) surface, VO_5H_5, $V_2O_9H_8$, $V_4O_{14}H_8$, $V_6O_{23}H_{16}$, $V_{10}O_{31}H_{12}$	C_3H_8	C_3H_6	B3LYP/6-31G*, B3PW91/6-31G*,SP with larger BS	2006[377]	TSR
$V_3O_7^+$	C_4H_8	C_4H_6	B3LYP/TZVP	2006[59c]	TSR
$V_4O_{10}^+$	CH_4	CH_3	B3LYP/TZVP	2006[59d]	SSR
V_4O_{10}	C_3H_8	C_3H_6	B3LYP/LACVP**:6-31G**	2007[378]	SSR
VO_3 clusters	C_3H_6	CH_3CHO, CH_2O, CH_2CHCHO, CH_3CH_2CHO, CH_3COCH_3	B3LYP/TZVP	2008[379]	SSR
$V_3O_6Cl_3$, M_3O_9 (M = Cr, Mo, W)	CH_4, C_2H_6, C_3H_8, $CH(CH_3)_3$	H-abstraction	B3LYP/LANL2DZ:6-31g**	2008[380]	
MO_x ($x = 1, 2, 3$) (M = Cr, Mo, W)	CH_4	$CH_3M(O)_{x-1}(OH)$, $CH_3MH(O)_x$	B3LYP/LACVP**:6-31g**	2002[381]	TSR
CrO_2^+	CH_4	$CrOCH_2^+$, CrO^+, $CrO(OCH_3)^+Cr^+$, $Cr(OH)_2^+$	B3LYP/TZVP_G(3df,2p)//B3LYP/DZVP, CCSD(T)/TZVP_G(3df,2p)//B3LYP/DZVP	2006[256]	TSR
CrO_2^+	CH_4	CH_3OH	B3LYP/6-311++G**	2006[382]	
CrO_2^+	C_2H_4	CH_2O	UB3LYP/6-311++G(3df,3pd)//6-311G(2d,p)	2006[383]	TSR
CrO_2^+	C_2H_4	C_2H_4O	UB3LYP/6-311++G(3df,3pd)//6-311G(2d,p)	2007[384]	TSR
$[M_2O_5(OH)]^-$ (M = Cr, Mo, W)	structures		B3LYP/ECP:6-311++G**	2003[13h]	
MnO, FeO	CH_4	CH_3OH	B3LYP/6-311++G**	2004[257]	SSR
MnS^+	CH_4	CH_3SH	B3LYP/6-311+G*	2006[385]	TSR
FeO^+	H_2	H_2O	B3LYP/Wachters:TZ2P, BP86/Wachters:TZ2P, FT97/Wachters:TZ2P	1998[386]	TSR
FeO^+	CH_4	CH_3OH, $FeCH_2^+$, $FeOH^+$	MP2/ECP-DZ	1992[261]	SSR
$FeO^{0/+/2+}$	CH_4	CH_3OH	B3LYP/Wachters:6-311G**	1998[387]	
FeO^+	CH_4	CH_3OH	B3LYP/Wachters:6-311G**	1999[388]	TSR
FeO^+, $Fe_2O_8H_4$, $Cu_2O_2(OH)(NH_3)_3$	CH_4	CH_3OH	B3LYP	2002[357]	TSR KIEs
FeO^+	CH_4	CH_3OH	B3LYP/Wachters:6-311G**CASSCF/6-311G**, SOC	2003[290]	TSR
$FeO(H_2O)^{2+}$	CH_4	CH_3OH	BP86/large STO set	2004[355]	SSR
FeO^+, Fe-ZSM-5	CH_4	CH_3OH	B3LYP/6-311G**	2006[389]	TSR
FeO^+	CH_3OH	CH_2O	B3LYP/Wachters:6-311G**	2000[20f]	TSR
FeO^+	arenes	phenol complexes	B3LYP/6-311G**	2008[390]	SSR
FeO^+, FeO^{2+}	isopentane	isomeric alcohols	B3LYP/Wachters:D95**	2001[391]	
FeO^+	norbornane	C−H	B3LYP/6-31g*	1999[392]	TSR
FeO^+	CO	$Fe^+ + CO_2$	B3LYP/6-311+G*	2005[41i]	SSR
FeO^+	CO	CO_2	DFT	2008[393]	TSR
FeO^+	C_2H_2	various oxidation products	B3LYP/DZVP(opt+3f):6-311++G(2d,2p)	2008[394]	TSR
$FeO_3^{\pm}$	CO	CO_2	BPE/Wachters-F:DZVP	2007[395]	SSR
FeO_4^{2-}, $HFeO_4^-$, H_2FeO_4	adamantane	adamantol	B3LYP/6-311++G**	2003[396]	

Table 8. Continued

$[M_m]^{-/0/n+}$	substrate	product(s)	level of theory	year	SSR/TSR/ MSR
FeO_2^+ (silica supported)	CH_4	CH_3OH, CH_2O	B3PW91, B3LYP 6-31G**, CRENBL, LANL2DZ, SRSC	2004[397]	SSR
FeO^+	CH_4	CH_3OH	B3LYP/6-311G**//B3LYP/3-21G*	1997[398]	TSR
FeO^+, MnO^+, CoO^+	CH_4	CH_3OH	B3LYP/Wachters:6-311G**	1998[399]	TSR
$L_5Fe^{IV}O^{2+}$	RH	R	B3LYP/LACV3P++**// LACVP	2007[248d]	MSR
$PorFeO(SH)^+$	CH_4	CH_3OH	B3LYP/ECP+LACVP:6-31G	2000[358]	TSR
P450	camphor	5-*exo*-hydroxycamphor	B3LYP/TZV:D95	2003[400]	TSR
FeS^+	CH_4	CH_3SH	B3LYP/6-311+G*	2001[401]	TSR
CoS^+	CH_4	CH_3SH	UB3LYP/6-311+G*	2007[402]	TSR
NiO	CH_4	CH_3NiOH	B3LYP/6-311++G(3df,3pd)	2009[403]	TSR
$(phen)CuO^+$ (phen = phenanthroline)	C_3H_8	$phenCuOH^+$, $phenCu^+$	B3LYP/TZVP	2004[283]	SSR
ZnO	CH_4	CH_2O, CH_3OH	CCSD(T)//B3LYP/6-311++G(2d,2p)	2006[404]	SSR
SrO^+	CH_4	CH_3OH	B3LYP/SDD:aug-cc-pVQZ//B3LYP/ SDD:6-311+G(2df,2p)	2008[405]	SSR
NbO, NbO_2, TaO, TaO_2	CH_4	$CH_3M(O)(H)$, $CH_3MO(OH)$	B3LYP/SDD:6-311++G**	2005[266]	SSR
Mo_3O_9	C_3H_8	C−H	B3LYP/LANL2DZ:6-31G	2005[406]	SSR
$Mo_2O_y^-$ ($y = 2-5$)	CH_4	$HMoO_2CH_3^-$	B3LYP/SDD	2007[407]	SSR
MoO_3^+	CH_4	CH_3	CASPT2D/ANO//B3LYP/D95, CASSCF/ANO// B3LYP/D95	1997[267a]	TSR
Mo_3O_9	CH_4	$Mo_3O_7(OCH_3)(OH)$	B3LYP/6-31g//B3LYP/LANL2DZ:6-31G**	2005[361]	SSR
$HRuOH^+$	CH_4	CH_3RuH^+	B3LYP/RECP:6-31+G**	2009[408]	TSR
MH^+ (M = Ru, Rh, Pd)	CH_4	CH_3M^+	B3LYP/RECP:6-31+G**	2009[409]	TSR
RhO	CH_4	CH_3OH	B3LYP/6-311+G(2d,2p)	2009[410]	TSR
PdO	CH_4	CH_3OH	LDA, B3LYP	1996[411]	SSR
Ag_2O^+	CH_4, C_2H_6, C_2H_4	CH_3, C_2H_5, C_2H_4O	B3LYP/SDD:6-311+G(2d,p)	2007[412]	SSR
LaC_n^+	benzene	$MC_xH_y^+$, $x = 2-18$, $y = 0-16$	B3LYP/LANL2DZ	2005[413]	SSR
LnO^+	C_4H_8	$ThOC_4H_8^+$	CCSD(T)/PP; CASSCF	1997[269]	SSR
OsO_n^+ ($n = 1 - 4$)	CH_4	$O_{n-1}OsCH_2^+$, $O_nOsCH_2^+$, $O_nOs(H)(CH_3)^+$	B3LYP/LANL2DZ:6-311G**	2004[272]	TSR
PtO^+	CO	$Pt^+ + CO_2$	UB3LYP/RECP:6-311+G(2d), MECP	2005[41i]	TSR
PtO	CH_4	CH_3OH	B3LYP/RECP:cc-pVTZ	2008[414]	
PtO_2^+	structure		various levels reaching from CASPT2/large TZ BS to B3LYP/LANL2DZ	2001[13f]	
M^+ (M = An)	CH_4		B3LYP/RECP:6-311++G(d,p)	2009[415]	TSR

[a] In a few cases, also related reactions with CO as a substrate are included for comparison, but the compilation is not at all comprehensive for this substrate.

endothermic and the reaction of CrO^+ is only slightly exothermic, which explains why these processes were not observed experimentally.[242a] The exothermicity of the reaction of MnO^+ with methane is already sufficient so that C−H bond activation takes place efficiently. The late transition-metal oxides FeO^+, CoO^+, and NiO^+ show the reactivity described above in detail for FeO^+. Finally, the reaction of CuO^+ can proceed without an intersystem crossing, because the whole reaction pathway in the triplet state is lying in energy below the reactants' asymptote. However, the ground state of the Cu^+ product is singlet; therefore, a spin flip is thermodynamically favored. Experimentally, however, the CuO^+ cation could not be produced in ion yields sufficient to probe its reactivity in the gas phase; generation of these simple diatomic cations is thus still an open challenge to gas-phase ion chemists in this area.

The C−H bond activation was further studied for larger systems, in which the iron-oxide cation bears additional ligands[355] or is coordinated in a larger environment such as P450.[356] It became clear that the four-center transition structure for the formation of the $CH_3-Fe-OH$ intermediate is energetically more and more demanding with increasing number of additional ligands on iron and instead the so-called "rebound mechanism" is involved.[353,357] This reaction mechanism starts with the hydrogen atom abstraction from methane by the oxygen atom of the L_nFeO^+ system. In the following reaction step, the methyl radical rebounds to the oxygen atom to directly form methanol. Further investigation of this reaction in models of P450 revealed that, even in the "rebound" mechanism, the reaction is associated with a spin-flip from the high-spin PES to the low-spin PES, where the rebound step proceeds without a barrier, which therefore renders the rebound process very fast (Figure 13).

As far as the mechanistic dilemma between a concerted two-electron process and a two-step rebound scenario is concerned, experimental studies point toward the occurrence of both pathways. For example, IR experiments of alkane activation on metal-oxide surfaces detected only closed-shell species containing alkoxy and hydroxy groups and, therefore, were interpreted as a proof for the concerted 2e-process.[359] On the other hand, the involvement

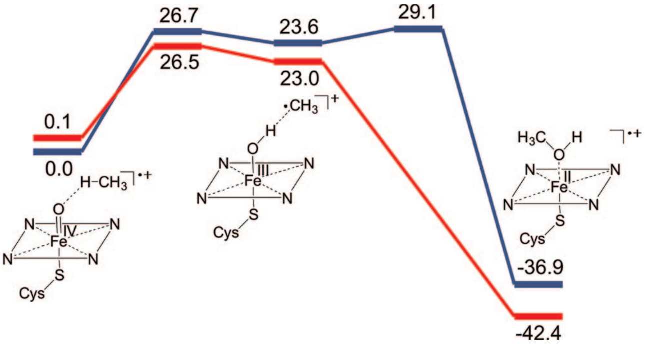


Figure 13. Potential-energy surface (in kcal/mol) for the model reaction of P450 with CH_4 in the doublet (red) and quartet (blue) states calculated at the B3LYP/LACVP:6-31G level of theory.[246d,358]

Table 9. Theoretically Studied Reactions of Various Metal Compounds (Neutral or Ionized) with Alkanes (Denoted as Substrate), the Major Products Investigated, the Method Used, the Year of Publication, and a Note Whether Single-State, Two-State, or Multistate Reactivity Has Been Investigated

$ML^{0/+}$	substrate	product	level of theory	year	SSR/ TSR/ MSR
L = H					
BH_3	CH_4, C_6H_6	CH_3, BH_2 C_6H_5, BH_2	B3LYP/6-311++G**	2000[418]	SSR
CaH^+, ScH^+−ZnH^+, SrH^+, ZrH^+−CdH^+, BaH^+, LaH^+, HfH^+−HgH^+	electronic structure		GVB	1990[419]	
MH^+ (M = Fe, Co, Ni)	CH_4	MCH_3^+	B3LYP/Wachters:cc-pVTZ	2004[217]	TSR
NiH^+	CH_4	$NiCH_3^+$	exploratory B3LYP	2007[206a]	
BaH^+, LaH^+, HfH^+−HgH^+	electronic structure		CI/HW:TZ	1990[420]	
PtH^+	CH_4	$PtCH_3^+$		2001[5g]	
$[Mg-CH_4]^+$, $[Mg-OC_2H_5]^+$, $[Mg-NH_2-CH_3]^+$	C−H		B3LYP/6-311++G**, MP2/6-311++G**, SP: CCSD(T)/6-311++G(d,pd)	2006[421]	SSR
$Ti(CH_4)_n$ ($n = 0-2$)	CH_4	$TiCH_2$, $Ti(CH_4)_n(CH_3)_2$	B3LYP/HW:6-311+G**//B3LYP/HW:6-31G**	1999[278b]	TSR
$FeCH_2^+$	H_2	Fe^+, FeH^+, $FeCH_3^+$	CASSCF/HW:6-31G, MR-SDCI-CASSCF	1994[112b]	TSR
MCH_3^+ (M = Fe−Ni, Ru−Pd, Os−Pt)	CH_4	MCH_3^+	B3LYP/TZVP/SDD	2008[205]	TSR
$Co(CH_4)_4^+$	binding energies		B3LYP/DZVP	2001[281]	
MCH_2^+ (M = Co, Rh)	H_2	CH_4	BP86/DZVP	1997[124c]	TSR
MCH_2^+ (M = Co, Rh, Ir)	H_2	CH_4	MR-SDCI-CASSCF	1993[124a]	
$PtCH_2^+$	electronic structure		relativistic effects	2000[8]	
$PtCH_2^+$	structure		HF, DFT, MP2, CCSD(T), relativistic effects	1996[422]	
$RhMCH_2^+$ (M = Pt, Rh)	NH_3	$[Rh,M,C,N,H_3]^+$	B3LYP/HW:6-31g*	2007[10c]	TSR
$LPtCH_3^+$ (L= aryldiimine)	H_2O, CH_3CN, CF_3CH_2OH	CH_4	B3PW91/SDD:6-31G**	2005[285c]	
$Pt_4CH_2^+$	O_2	HCOOH, CO + H_2O	BPW91/TZ(2)P-STO, relativistic effects, ZORA	2007[423]	SSR
$PtMCH_2^+$ (M = Cu, Ag, Au, Pt)	NH_3	$PtMNHCH_2$	BPW91/TZ2P	2006[424]	
$Fe(CH_2O)^+$, $Fe(CH_2S)^+$	structure, electronic states		B3LYP/WachtersH:6-311G*//B3LYP/HW:DZ adduct	1997[230]	
$Fe(C_6H_4)^+$	C_6H_6		B3LYP/LANL2DZ:6-31G(d)	2000[425]	
$Fe_2O_2(HCOO)_2(NH_2)_2(H_2O)_2$, $Fe_2O_2(HCOO)_2Fe(Im)_2(HCOO)_2$ (Im = imidazole)	CH_4, C_2H_6, CH_3F, C_2H_4	CH_3OH, C_2H_5OH, $CH_2(OH)F$, CH_2H_4O	B3LYP/SBK(+dC,N,O)//B3LYP/CEP-31	2002[426]	SSR
$Fe_2O_2(HCOO)_2(NH_2)_2(H_2O)_2$	CH_4	CH_3OH	B3LYP/SBK(+dC,N,O)//B3LYP/CEP-31	2001[427]	TSR
$[FeO\cdot EDTAH_n]^{(2-n)+}$	CH_4	CH_3	BLYP/TZ2P, OPBE/TZ2P	2008[428]	SSR
model for hydroxylase component of methane monooxygenase	CH_4	CH_3OH	B3LYP/LANL2DZ	2001[429]	SSR
hydroxylase component of methane monooxygenase	CH_4, C_2H_6, CH_3OH, CH_3CN, CH_3NO_2, CH_3F	CH_3, C_2H_5, CH_2OH, CH_2CN, CH_2NO_2, CH_2F	QM/MM QM: B3LYP/LACV3P**:cc-pVTZ(-f)// B3LYP/LACVP**:6-31g**	2005[430]	SSR
model for hydroxylase component of methane monooxygenase	CH_4	CH_3	B3LYP/LACV3P**:cc-pVTZ(-f)//B3LYP/ LACVP**:6-31 g**	2005[431]	SSR
$CpCo^+$	$2CH_4$	$C_2H_6 + H_2$	B3LYP/LACV3P**+//B3LYP/ LACVP**	2000[231b]	SSR
$CpCo^+$	CH_4	$(C_7H_{11})Co^+ + H_2$	B3LYP/LACVP	2004[231a]	SSR
$[CpM(PH_3)]$ (M = Co, Rh, Ir)	CH_4	$[CpM(PH_3)(CH_3)H]$	B3LYP/LACVP**:6-311G** MECP	2006[293]	TSR
LCu^+, LCu^{2+} (L = NH_3, PH_3, $(CH_3)_2O$)	CH_4	C−H	LCAO-SCF-MO SP: MRCI	1993[432]	SSR
LMCl (M = Rh, Ir; L= 1,3-$(CH_2PH_2)_2$-2-CH_3-C_6H_3)	C−H and C−C within the complex		B3LYP/ECP:6-31g**	2000[433]	SSR
$PdCl^-$	H_2, CH_4, C_2H_6, CH_3Cl	C−H, C−C	BP86/TZ(2)P-STO, relativistic effects, ZORA	2005[434]	SSR
cis-$Pd(CO)_2I_2$	H_2, CH_4, C_2H_6, CH_3I	C−H, C−C, C−I	BP86/TZ(2)P-STO, relativistic effects, ZORA	2005[435]	SSR
$Pt(L)(H_2O)(CH_3)^+$, L = HN=CH−CH−NH	CH_4	$LPt(H)(CH_3)_2(H_2O)$	BP86/fc-TZV:DZVP, LANL2DZ:6-31G**	2000[436]	SSR
$LPtX^+$ (X = H, Me, C_6H_5), L= aryl diimine	CH_4, C_6H_6	C−H	B3PW91/SDD:6-31G**	2007[437]	SSR
$(C_5H_5)M(L)$ (M = Rh, Ir; L = CO, PH_3) and $M(CO)_4$ (M = Ru, Os)	CH_4	$(C_5H_5)M(L)(CH_3)(H)$, $M(CO_4)(CH_3)(H)$	LCAO-HFS, TZ-STO	1989[438]	SSR

of radical species in the reaction of tungstated zirconia catalyst with pentane was shown by EPR experiments, which therefore favored the rebound mechanism.[360] A nice example of a theoretical contribution to this discussion represents a study of the methane oxidation by molybdenum oxides (Figure 14).[361] The catalyst was modeled by a Mo_3O_9 cluster, and the results showed that the rebound mechanism leads via a lower energy pathway and therefore is favored. However, the minimum representing the radical-pair intermediate is very shallow, and therefore, the lifetime of this intermediate is anticipated to be very short. These results thus provide a rationale for all experimental findings: Due to the short lifetimes of the radical pair, the IR spectra show only the products, whereas the EPR experiment is able to selectively detect the intermediate radicals.[361]

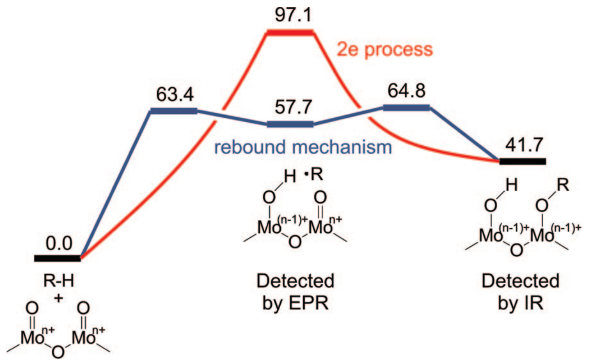


Figure 14. Potential-energy surface (in kcal/mol) for the model reaction of Mo_3O_9 with hydrocarbon RH (calculated for methane) at 873 K calculated at the B3LYP/LANL2DZ:6-31G** level of theory.[361]

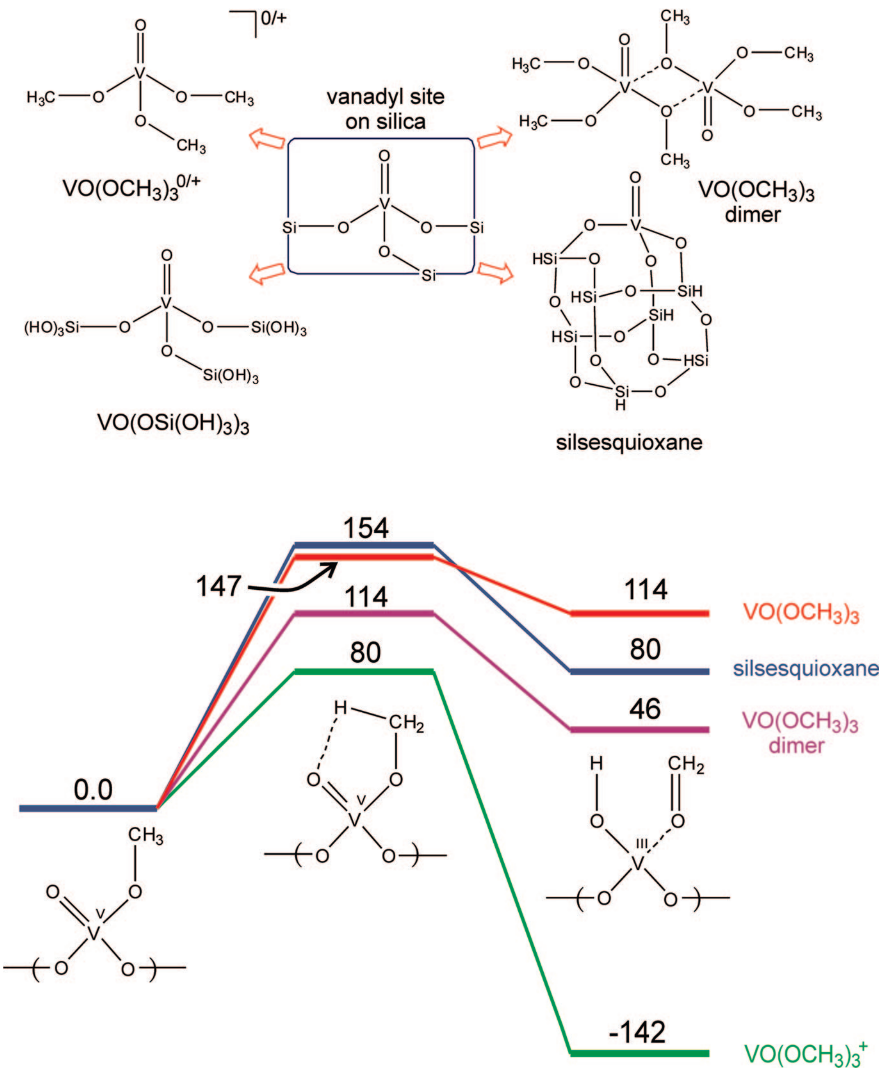


Figure 15. Different models for a vanadyl site of a silica-supported vanadium-oxide catalyst and the comparison of thermodynamics and energy barriers (in kJ mol^{-1}) for the oxidation of the methoxy group calculated within different models using B3LYP/TZVP.[374]

5.5. Catalytically Active Sites: A Real Catalyst Modeled by Metal Clusters

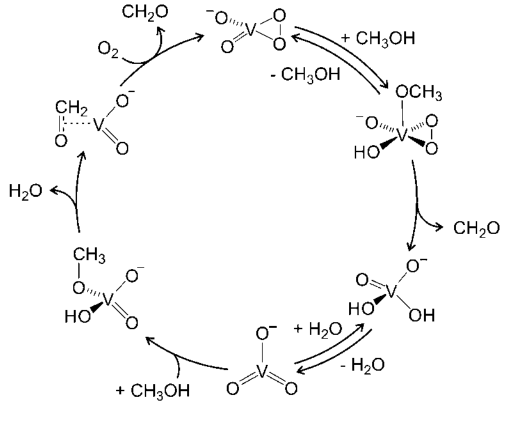
Due to obvious reasons, the numerous mass spectrometric studies on hydrocarbon oxidation with metal catalysts rely on charged models of the catalytic sites. One of the big advantages of the accompanying theoretical studies is that they are not limited by the charge requirement and they can build more complicated as well as more sophisticated models for the catalytic sites. An example of reactions studied in detail using mass spectrometry and quantum chemistry are oxidations of hydrocarbons and their derivatives on silica-supported vanadium oxide. In this context, we include one example about the oxidation of methanol to formaldehyde because it is considered particularly instructive for the interplay between experiment and theory on model systems. The mass spectrometric studies rely on $VO(OCH_3)_3^+$ and larger clusters such as $V_3O_7^+$ and $V_4O_{10}^+$.[19,45,46,59c,d] Theoretical studies are used in concert to interpret the data and provide a deeper insight, but they can be used also to estimate the relevance of a certain model with respect to real catalysis.

The $VO(OCH_3)_3$ molecule represents a minimal model for an intermediate formed in the oxidation of methanol at a vanadium-oxide site of a silica-supported catalyst. In the first step of the reaction sequence, the molecule of methanol is adsorbed on the surface of the catalyst with an envisaged structure VO(O−Si−)$_3$ (Figure 15). The absorption is associated with the cleavage of one of the V−O−Si bridges and provides $VO(OCH_3)$(O−Si−)$_2$ and HOSi− sites. In the following step, a hydrogen atom from the methoxy group is transferred to the vanadyl-oxygen atom, which results in formation of formaldehyde. $VO(OCH_3)_3$ thus represents an intermediate, in which two methoxy groups stand for the missing O−Si links to the silica support while the remaining part is realistic. In the singly charged state, the model corresponds to the V^{V} oxidation state with a radical site located at the oxygen atom and the rearrangement leads to the V^{IV} radical species coordinated to formaldehyde (Figure 15). The overall reaction within this radical cationic model is exothermic. The energy barrier predicted at the B3LYP level (~80 kJ mol^{-1}) is slightly overestimated, as revealed by the comparison with the threshold photoionization study of dissociation of $VO(OCH_3)_3^+$, which suggests a barrier of about (52 ± 10) kJ mol^{-1}. The same model reaction in the neutral state shows very similar results as far as the geometry of intermediates is concerned. However, the oxidation states of intermediates and products are V^{V} and V^{III}, respectively, and the corresponding reaction step is *endothermic*, precisely as experiments with real catalysts suggest. Thus, we can conclude that, in this case, the charged model can provide hints with respect to the reaction mechanism and suggest the structures of intermediates but cannot be taken as a reliable guidance for energetic considerations.[375] Finally, it has to be noted that the transition structure for the hydrogen migration from the methoxy group to the oxygen atom has a biradicaloid character, which has to be acknowledged by the calculations. In the present case, a broken-symmetry approach has been chosen.[375]

If we further test the relevance of such simplified models, we can compare the $VO(OCH_3)_3$ model with larger molecules such as a dimer of $VO(OCH_3)_3$, $OV[OSi(OH)_3]_3$, or vanadyl silsesquioxane (Figure 15). The dimer of $VO(OCH_3)_3$ shows a reactivity analogous to that of the monomer, except that the endothermicity of the oxidation as well as the relevant reaction barrier are smaller. The next two models, $OV[OSi(OH)_3]_3$ and silsesquioxane, offer the possibility to study also the first reaction step, i.e. the absorption of methanol on the catalyst. This step leads in the case of the $OV[OSi(OH)_3]_3$ catalyst to free $Si(OH)_4$, which is stabilized by a formation of intramolecular hydrogen bonds.[376] This degree of freedom is not present in a real catalyst, and therefore, this model exaggerates the absorption energy (88 kJ mol^{-1}). In the case of the vanadyl-silsesquioxane complex, the addition of methanol to the model catalyst is associated with the formation of an integrated $-O-Si(H)(OH)-O-$ unit, and therefore, the results can be expected to be more accurate. Accordingly, the absorption energy drops by more than one-half to 40 kJ mol^{-1}. The next step consists in the hydrogen rearrangement within the $-O-VO(OCH_3)-O-$ unit. The activation energy for this step is calculated as 199 kJ mol^{-1} for the $OV[OSi(OH)_3]_3$ model and 202 kJ mol^{-1} for silsesquioxane. These values bear, however, large errors, because they are obtained within the closed-shell approximation. The optimization using the broken-symmetry approach and correction for the spin-contamination leads finally to a value of 170 kJ mol^{-1} and the inclusion of zero-point vibrational energy further lowers the energy barrier to 154 kJ mol^{-1} (Figure 15). It has been shown by the authors that these results are in very good agreement with the experiments made with a real system, and therefore this model appears as adequate.[375] However, we can see that the much more simple model $VO(OCH_3)_3$ is also capable of providing valuable results for the second reaction step, albeit it requires much less computational effort.

A completely different approach to the same reaction has been taken by Waters et al.,[372,373] who not only used the very simple model of VO_3^- to experimentally mimic the oxidation of methanol to formaldehyde, but they were also able to provide experimental data about the reoxidation of the catalyst. The first step of the reaction corresponds to the addition of methanol so that the methoxy group binds directly to the vanadium atom and the hydrogen atom binds to one of the oxygen atoms of VO_3^- (Scheme 13). In the second step, another hydrogen atom from the methyl group migrates to the hydroxyl group, which leads to a complex of VO_2^- and molecules of water and formaldehyde. This complex preferentially loses the water molecule. The formaldehyde is subsequently exchanged by molecular oxygen, and this step therefore represents the reoxidation of V^{III} back to the V^V catalyst. The following absorption of another methanol molecule proceeds in analogy to the first step, but the oxidation of the methoxy group to formaldehyde is this time not associated with the formation of a water molecule but with the reduction of the η^2-peroxy ligand. Elimination of the so-formed formaldehyde molecule then leads to a restoration of the initial VO_3^- species, thereby completing the catalytic cycle. Detailed B3LYP studies provided structures of all intermediates and explained the preferential loss of water after oxidation of the first methanol molecule. The same reaction with ethanol leads to production of the analogous products in the reaction cycle, i.e. water and acetaldehyde, but there is an additional channel, which even dominates and leads to the formation of ethylene.[373,416] It has to be noted that the calculated energetics are not in a direct relation with the experiments conducted with real catalysts, but this model is important, because it shows a possible mechanism for the reoxidation step.

Scheme 13. Catalytic Cycle for the Oxidation of Two Molecules of Methanol with One Molecule of Oxygen[372]



Another broad area—as far as the selection of a proper model for the investigation of reaction mechanisms at the molecular level is concerned—represents the ODH of propane on supported (SiO_2, TiO_2, Al_2O_3) vanadium catalysts. A comprehensive theoretical study provides detailed information of individual reaction steps using VO_5H_5, $V_2O_9H_8$, $V_4O_{14}H_8$, $V_6O_{23}H_{16}$, $V_{10}O_{31}H_{12}$, and V_2O_5 (010) surfaces as model catalysts (Figure 16). The relevance of the smallest models, VO_5H_5 and $V_2O_9H_8$, for the description of the elementary reaction steps was probed by comparison with the results obtained with larger clusters and periodic calculations with a V_2O_5 (010) surface. The authors showed that the proper model for a catalyst is important, because inappropriate termination groups can lead to an artificial increase of reactivity.[417]

6. Regioselective Gas-Phase Activation of Alkanes

In this section, we discuss some examples out of the above compilation which provide insight into the selectivitities of the reactions of gaseous ions in alkane activation. In this respect, we differentiate between chemoselectivity, i.e. C−H- versus C−C-bond activation of alkanes, regioselectivity, i.e. activation of different C−H bonds, and diastereoselectivity in C−X-bond activation (X = H, C, Si).

6.1. Chemoselectivity

In many of the reactions listed above, for larger alkanes a competition between C−H- and C−C-bond activation is observed. Out of the many examples, the studies of Tjelta and Armentrout are particularly insightful, in which the branching between dehydrogenation and demethanation of propane by ligated $Fe(L)^+$ cations (reactions 12 and 13) has been investigated by ion-beam methods.[229]

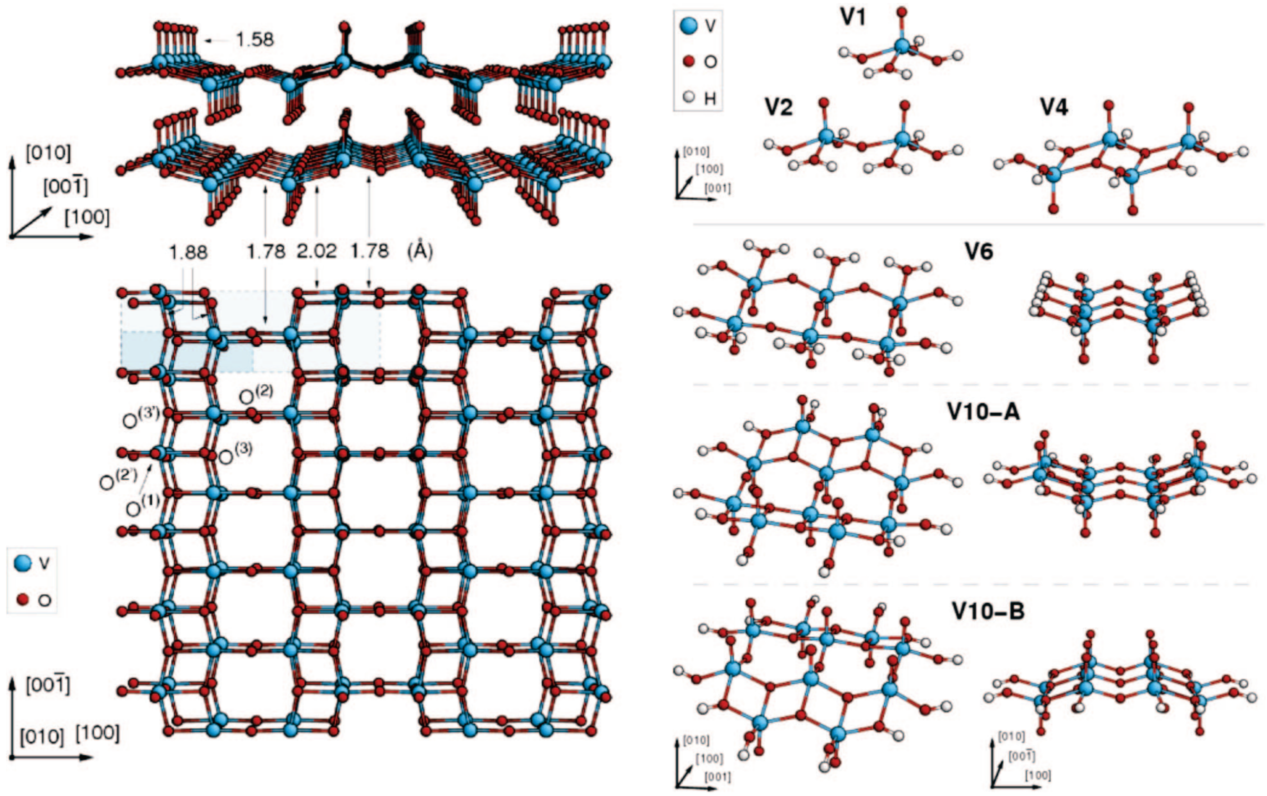


Figure 16. Structure of cluster models used to represent the (010) surface of V_2O_5: **V1** = VO_5H_4, **V2** = $V_2O_9H_8$, **V4** = $V_4O_{14}H_8$, **V6** = $V_6O_{23}H_{16}$, and **V10-A** (**V10-B**) = $V_{10}O_{31}H_{12}$ (**V10–B** is inverted **V10-A**). Reprinted from ref 377.

Table 10. Relative Rate Constants and Selectivities for C–H- and C–C-Bond Activation of Propane by $Fe(L)^+$ Cations[a]

	k_{rel}	S_{C-H}	S_{C-C}
Fe^+	1.00	25	75
$Fe(CO)^+$	0.02	90	10
$Fe(H_2O)^+$	0.80	5	95

[a] Approximate values derived from the lowest-energy points in Figure 1 in ref 229b.

C–H activation:

$$Fe(L)^+ + C_3H_8 \rightarrow Fe(L)(C_3H_6)^+ + H_2 \qquad (12)$$

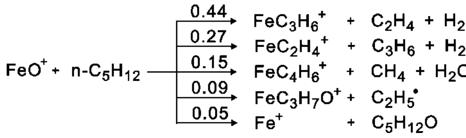
C–C activation:

$$\rightarrow Fe(L)(C_2H_4)^+ + CH_4 \qquad (13)$$

The first significant observation to be made is that both ligands tested (L = CO and H_2O) lower the overall reactivity compared to that of the bare metal (k_{rel} normalized to Fe^+). While the effect is dramatic in the case of the carbonyl ligand (a strong π-acceptor ligand), the decrease for water (a weak π-donor ligand) is moderate. More interesting than the decrease in overall rate is the change in selectivity (Table 10). Thus, the 25:75 ratio between reactions 12 and 13 in the case of bare Fe^+ is inverted to 90:10 for $FeCO^+$ in favor of C–H-activation, whereas the water ligand promotes C–C-bond cleavage. A theoretical rationale for these remarkable experimental observations still is to be provided.

Similar ligand effects have been observed in the reactions of many other ligated transition-metal cations with alkanes, most often with the result that additional π-ligands (e.g., CO, alkenes, etc.) quench the reactivity of the metal ions toward alkanes. This behavior is in marked contrast to that of many covalent ligands X, which change the formal oxidation state of the metal center and hence the entire electronic situation, while coordinative ligands L only modify it (see above). Accordingly, the effects of covalent ligands in MX_n^+ cannot be classified in simple terms, and compared to the bare metal ion, the MX_n^+ species can be much less or much more reactive (see Tables 4 and 5).

Scheme 14. Branching Ratio in the Reaction of *n*-Pentane with the FeO^+ Cation



As an example of such species with covalently bound ligands, we consider the chemoselectivity in the reactions of transition-metal oxide ions with hydrocarbon substrates, which again is crucially influenced by ligation. The bare FeO^+ cation, for example, reacts with various hydrocarbons via several C–H- and C–C-bond activation pathways. In the reaction with a still reasonably simple substrate such as *n*-pentane with three types of different C–H bonds and two different C–C bonds, FeO^+ leads to no less than five different products (Scheme 14). In marked contrast, the corresponding complexes with arene ligands, $(L)FeO^+$ with L = benzene, naphthalene, and pyridine, show much larger selectivities.[439] With olefins, for example, O-atom transfer occurs almost exclusively. The price to pay for the increased selectivity is a considerable loss in reactivity, however. Thus, while bare FeO^+ is capable of activating even methane, the ligated ions do not any longer react with alkanes at measurable rate constants and only unsaturated substrates undergo oxidation. In the context of partial oxidation of alkanes, another important aspect with regard to chemoselectivity is that the reactive species which can bring about activation of the alkane usually reacts much faster with the primary oxidation products (e.g., alcohols or olefins). Thus, the reaction of FeO^+ with methane has about 10% efficiency, whereas the corresponding oxidation of methanol occurs at the collision rate.[20e]

6.2. Regioselectivity

In contrast to the large number of experimental and theoretical studies about the activation of alkanes and related hydrocarbons, much less has been done with respect to regioselectivity. In fact, in the large body of studies concerning the metal-ion mediated dehydrogenation of alkanes, in many cases even the site of the initial C−H-bond activation is not known experimentally. In this respect, let us address the dehydrogenation of propane by atomic Co^+ cations as an example. Labeling data and cross section measurements indicate a notable kinetic isotope effect upon deuteration of the primary C−H bonds, which has accordingly been assigned as the rate-determining step.[129] This interpretation somewhat conflicts with the lower KIE of the competing methane-loss channel, for which also insertion into primary C−H bonds has been proposed as being rate-limiting. Instead, Armentrout and co-workers concluded that there exists a competition between the activation of primary and secondary C−H bonds and the final dehydrogenation as the rate-determining step.[130a] Also, extensive theoretical work does not provide a clear answer to the question of the selectivity of the initial insertion process, because the error of the predictions is larger than the energy difference of the competing channels. Thus, Holthausen and co-workers found initial insertion into a secondary C−H bond to be preferred by 35 kJ mol^{-1}, but the experimental data required an adjustment of the computed barriers by some 20 kJ mol^{-1}.[130b] In contrast, Fedorov and Gordon reported a difference of only 13 kJ mol^{-1}, and in their calculations all TSs are significantly lower in energy with respect to the separated reactants.[131b] Hence, despite the wealth of both experimental and theoretical information available for the Co^+/C_3H_8 system, the selectivity of the insertion process still remains unknown. Part of these difficulties is, however, associated with the fact that in a dehydrogenation two hydrogen atoms are involved and the specific deuterations thus affect several elementary steps at the same time.

More direct experimental information about selectivities in alkane activation has been achieved from various reactions of metal-oxide ions in which H-atom abstraction is observed. The formal copper(III) compound $(phen)CuO^+$, for example, shows a 40:60 selectivity in the activation of the primary and secondary C−H bonds of propane.[283] A similar selectivity of 44: 56 has been found for H-atom abstraction from propane by the disilveroxide cation Ag_2O^+.[412] In contrast, extensive kinetic modeling implied that in the case of propane activation by the iron-oxide cation FeO^+ attack of primary C−H bonds is preferred (77:23).[20d] If rescaling these experimental data to the number of primary and secondary C−H bonds in propane, we arrive at ratios for attack of primary and secondary C−H bonds of $1°/2° = 18:82$ for $(phen)CuO^+$, 21:79 for Ag_2O^+, and 53:47 for FeO^+. Thus, FeO^+ attacks more or less randomly, whereas the two former oxide cations show considerable selectivities for secondary C−H bonds. In the case of isobutane and $(phen)CuO^+$, the corresponding ratio for attack of primary and tertiary C−H bonds amounts to even $1°/3° = 2:98$. Yumura and Yoshizawa studied the regioselectivity for the activation of 2-methylbutane by FeO^+ and FeO^{2+} by theoretical means and predicted a preferential activation of secondary C−H bonds for concerted mechanisms, whereas radicaloid scenarios predominantly involve the tertiary C−H bond of the substrate.[391]

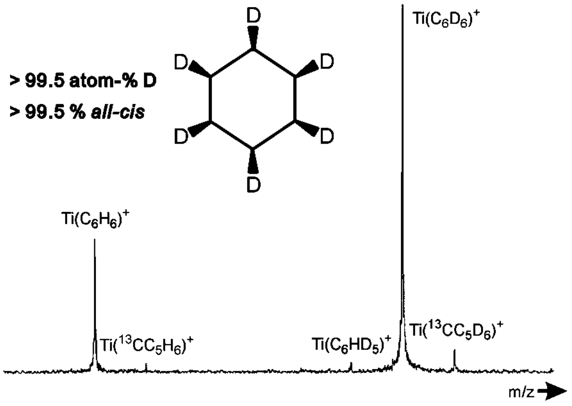


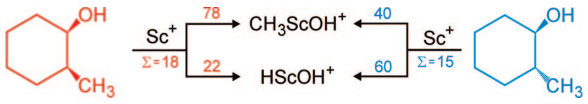
Figure 17. Triple dehydrogenation of cyclohexane to the corresponding benzene complexes in the ion/molecule reaction of mass-selected Ti^+ cations with [*all-cis*-1,2,3,4,5,6-D_6]-cyclohexane.

6.3. Diastereoselectivity

Despite the huge importance of transition-metal catalysts in asymmetric synthesis, there so far exist only very few reports about stereoselective reactions of gaseous metal ions in general and even less about such effects in the bond activation of alkanes.[440,441] In this respect, the late Ben S. Freiser initiated a fascinating research project centered about the use of metal-mediated dehydrogenation reactions in a mass spectrometer for the analysis of the diastereospecifity of hydrogenation catalysts.[442] With respect to this specific analytical application, the use of early transition metals is of advantage because the dehydrogenations occur fast, completely, and with minimal H/D scrambling. As an example, Figure 17 shows the mass spectrum obtained for the reaction of mass-selected Ti^+ with a deuterated cyclohexane sample.[86] From the analysis of the data, we can conclude that the sample has more than 99.5 atom % D and also that more than 99.5% is the *all-cis* configuration. Literally, the Ti^+ cation acts like a razor upon approach of the cyclic alkane and rapidly promotes triple dehydrogenation of one side of the cyclohexane to the corresponding arene. For the *all-cis* deuterated compound, this means that either unlabeled $Ti(C_6H_6)^+$ or the fully deuterated ion $Ti(C_6D_6)^+$ is formed; the larger abundance of the latter is a consequence of the kinetic isotope effects operative in the 3-fold losses of H_2 and D_2, respectively. The results shown in Figure 17 simultaneously imply that the combined diastereoselectivity of all three dehydrogenation steps exceeds 99.5%. While almost identical results are obtained with Sc^+, the later 3d metal cations cannot afford a complete 3-fold dehydrogenation of the substrate or even do not promote C−H bond activation at all. Further, in the cases of Fe^+, Co^+, and Ni^+ also, significant losses of HD are observed, which imply that either the metal can change the site during the reaction (e.g., via insertion in a C−C of the ring followed by reductive elimination) or inner-sphere electron transfer processes give rise to H/D equilibration reactions.[71]

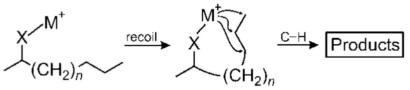
We note in passing that even a diastereoselective C−C bond activation has been observed in the related Sc^+ cations with 2-methylcyclohexanol. Experimentally, it is found that the ratio of the C−O-bond insertion/β-group transfer products CH_3ScOH^+ and $HScOH^+$ is in favor of the former for the *syn*-diastereomer (Scheme 15).[311] These results strongly point

Scheme 15. Diastereoselective C−C Bond Activation of 2-Methylcyclohexanol for the *cis*- (Red) and *trans*-Isomers (blue) by Gaseous Sc^+ Cations[a]



[a] The numbers above the arrows indicate the ratios of the insertion products CH_3ScOH^+ and $HScOH^+$, respectively, and the sums below the arrows represent the overall yield of these products in the ion/molecule reaction of Sc^+ with the substrate. Other products are ScO^+ and $ScOH^+$ as well as $ScC_6H_6O^+$ and $ScC_7H_8O^+$, where the two latter are formally due to triple dehydrogenation or double dehydrogenation/demethanation to the corresponding arenes, respectively.

Scheme 16. Sketch of the Recoil Mechanism of the Alkyl Chain in Complexes of Monofunctionalized Alkanes and a Metal Cation[a]



[a] The ring-size and geometric constraints of both the metal M and the functional group X determine which C−H bond activation pathway is followed preferentially en route to product formation.

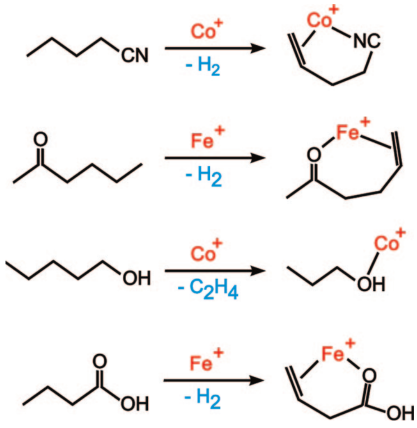
toward a concerted *syn*-1,2-elimination of R and OH (R = H, CH_3) from the alkanol or—by reference to the concept of microscopic reversibility—a *cis*-orientation in the reverse reaction, i.e. the addition of $RScX^+$ across a C−C double bond.

6.4. Remote Functionalization of Heterosubstituted Alkanes

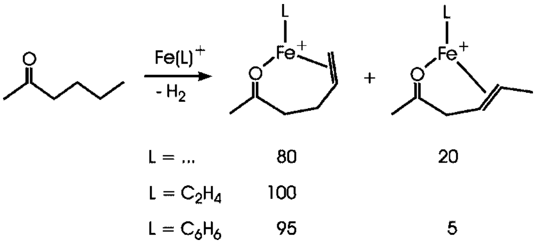
A particularly interesting topic of C−H bond activation with direct implications for synthetic protocols as well as biochemical processes deals with the activation of remote C−H bonds in monofunctionalized alkanes. These molecules consist of a functional group X and an alkyl chain in which the position(s) where the C−H bond activations occur is mass spectrometrically best traced by means of selective deuterium labeling. In the interaction with the metal ion, the functional group X serves as an anchor for docking of the metal in a certain position. This initial fixation of the metal at the functional group is followed by recoil of the alkyl chain in which the coordination geometry of the metal in conjunction with the flexibility of the various bonds involved determines the C−H bonds to be activated preferentially (Scheme 16). In analogy to Breslow's time-honored concept of remote functionalization,[443,444] these reactions have been termed as the gas-phase variant of remote functionalization.[445]

This type of reaction has first been observed in a study of Tsarbopoulos and Allison about chain-length effects in reactions of n-C_nH_{2n+1}-X compounds (X = H, Cl, OH) with Co^+ ions which revealed an increased amount of dehydrogenation for longer alkyl substituents.[446] At that time, the reaction could not be clearly identified because no labeled substrates were available. Carlito Lebrilla, a postdoc in the group of H. Schwarz at the TU Berlin with experience in C−H bond activation from his work with R. H. Crabtree, proposed that activation of remote bonds in the alkyl substituents may be involved. Via synthesis of appropriately deuterated nitriles, it could then be shown that indeed remote C−H and C−C bonds are cleaved in the fragmentation reactions of metastable alkanenitrile/Fe^+ complexes.[25b] In the following, this proof of concept has been tested on a variety of late 3d metal compounds (e.g., nitriles, ketones, alkanols, and acids, Scheme 17) as well as metals, where the latter mostly belonged to the late 3d series.[447]

Scheme 17. Representative Examples for the Activation of Remote C−H and C−C Bonds of Monofunctionalized Alkanes by Bare Transition-Metal Cations



Scheme 18. Ligand-Dependent Selectivity for the Activation of Remote C−H Bonds in 2-Hexanone/Fe(L)$^+$ Complexes



By means of extensive deuteration studies, also including double labeling experiments, not only the precise regiochemistry could be elucidated, but quasi as a byproduct also some quite detailed insight into the mechanisms of the C−H- and C−C bond activation were achieved, which inter alia contributed to the doubts which were cast against the classical conception of this reaction via a dihydrido intermediate (see Scheme 6 above). The detailed insight was possible primarily because the activation barriers associated with remote functionalization of monofunctionalized alkanes by bare metal ions are particularly low. For the remote dehydrogenation of ketones in their Fe^+ complexes, for example, a barrier height on the order of 50 kJ mol^{-1} has been derived from ligand-dependent reactivity studies.[239c] Ligand effects can also be used to direct the selectivity in the activation of remote C−H bonds (Scheme 18).[239a,b]

The broad variety of substrates and metals which so far have been shown to undergo remote functionalization in the gas phase are compiled in Table 11.

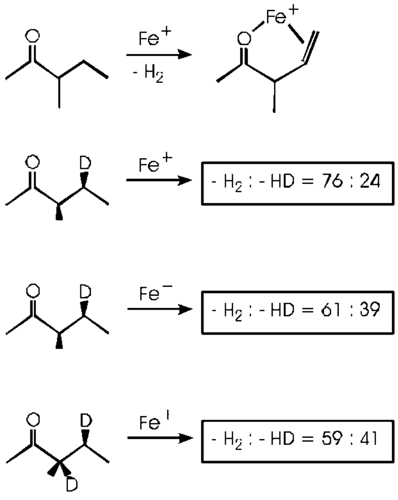
The low activation barriers associated with the remote functionalization of monofunctional alkanes by bare metal cations in conjunction with the large selectivities also opened the route toward diastereoselective C−X bond activations (X = H, C, Si). As an example of the corresponding entries in Table 11 in which a significant steric effects (denoted as SE in Table 11) have been observed, we refer to the Fe^+ complexes of 3-methyl-pentan-2-one.[452] Like for other ketone/Fe^+ complexes, unimolecular dissociation of the metastable ions leads to a highly selective 4,5-dehydrogenation. While the 3-methyl group is itself not involved in bond-activation processes, it can serve as a stereochemical marker and thereby allow the diastereoselective introduction of deuterium

Table 11. Metal Ions and Substrates for Which the Functionalization of Remote Bonds Has Been Observed and Sufficiently Substantiated by Either Experiment or Theory[a]

$[M]^{-/0/+}$	substrate	process(es)	method	comments	year
M^+	nitriles	C−H, C−C	MI	M = Fe−Ni	1987[25b,448]
M^+	nitriles	C−H, C−C	ICR	M = Mn−Ni	1988[449]
M^+	nitriles	C−H, C−C	MI	M = Mn−Ni	1991[450]
Fe^+	1,8-octanediol	C−H	MI	KIE	1991[451]
Fe^+	methylpentanone	C−H	MI	SE, KIE	1993[452]
Fe^+	ketones	C−H, C−C	ICR		1981[453]
Fe^+	ketones	C−H, C−C	MI	2-fold reaction	1989[24,454]
Fe^+	ketones	C−H, C−C	MI	KIE	1991[455]
Fe^+	ketones	C−H, C−C	MI	Ingold−Thorpe	1991[456]
Fe^+	carboxylic acids	C−H, C−C	MI	SE, KIE	1994[457]
Fe^+	valeramide	C−H	MI	SE, KIE	2002[458]
Fe^+	aldimines	C−H, C−C	MI		1990[459]
Fe^+	butyronitrile	C−H, C−C	MI		1990[460]
Fe^+	valeronitrile	C−H, C−C	MI, ICR		1991[461]
Fe^+	*n*-alkanenitriles	C−H, C−C	MI	KIE	1989[462]
Fe^+	*n*-alkanenitriles	C−H	MI + theory	selectivity	1997[327]
Fe^+	branched nitriles	C−H, C−C	MI	2-fold reaction	1989[454a,463]
Fe^+	^{t}Bu-nitriles	C−H, C−C	MI		1988[464]
Fe^+	silyl-nitriles	C−H, C−Si	MI		1990[465]
Fe^+	alkenenitriles	C−H, C−C	MI		1989[466]
$FeCH_3^+$	*n*-alkanenitriles	C−H, C−C	ICR		1994[467]
FeO^+	ketones	C−H, C−C	ICR	ODH	1990[468]
Co^+	*n*-hexanol	C−H, C−C	MI		1991[469]
Co^+	*n*-alkanenitriles	C−H	MI + theory	selectivity	1997[327]
Co^+	nitriles	C−H, C−C	MI	SE, KIE	1995[470]
Co^+	silyl-nitriles	C−H, C−Si	MI	SE, KIE	1997[471]
Ni^+	amino acids	C−H, C−C	MI		1997[472]
Cu^+	octyne	C−H, C−C	MI, ICR		1992[473]
Cu^+	nitriles	C−H, C−C	MI		1987[474]

[a] For abbreviations, see footnotes to Table 3.

Scheme 19. Diastereoselective Activation of Remote C−H Bonds in 3-Methylhexan-2-one/Fe^+ Complexes



labeling. Thus, for the compound with *syn*-orientation of the 3-methyl group and the deuterium atom, a higher preference for loss of H_2 is observed than for the corresponding complex with an *anti*-arrangement of the 3-methyl group and the deuterium label (Scheme 19).

Quantitative analysis of the H_2/HD ratios in Scheme 19 using a simple kinetic model reveals a kinetic isotope effect of KIE = 2.1 and a stereochemical effect of SE = 1.5 for this particular combination of metal and substrate. While the diastereoselectivity is not spectacular, the case outlined in Scheme 19 was the first example of a diastereoselective gas-phase reaction in a flexible alkyl chain (Table 12).

In 1997, the extensive experimental work on remote functionalization was combined with the new developments of theoretical methods—the "*invasion of DFT*" in particular. Thus, Holthausen used a combined ab initio molecular modeling approach for a detailed investigation of the remote functionalization of alkanenitriles by Co^+ cations.[327] While some small details were not fully addressed, the general concept and the observed gross selectivities were pleasingly well explained by the theoretical model. The fundamental mechanisms of remote functionalization in the gas phase were hence clarified, and thus, the efforts ended with a success story. Nevertheless, we may ask why the promising concept has not been pursued further and why other research areas have not adopted the ideas and strategies developed in the course of this research. In a nutshell, the answer is that the concept is attractive as an idea, but the transfer from the mass spectrometric scale to bulk processes rapidly turned out to be impossible. Thus, not only are most of the metal ions in the unrealistic oxidation state M^I, but moreover in almost all cases when additional ligands were added, the ability of the complexes to activate either C−H or C−C bonds was quenched completely. This finding can be understood by the fact that the major driving force for the occurrence of the gas-phase variant of remote functionalization is the coordinative unsaturation of the metal cation; more realistic coordination spheres consequently lead to a complete loss of reactivity toward nonactivated C−H bonds. Notwithstanding, within the context of remote functionalization by bare metal ions, some analytical applications have been developed.[475]

7. Selective C−H Bond Activation by Transition-Metal Cluster Ions

This section briefly presents the reactions of metal clusters which fall within the scope of the present review.[476,477] In fact, a very large number of metal clusters can activate alkanes; however, quite often excessive dehydrogenation is observed,

Table 12. Kinetic Isotope Effects (KIEs) and Stereochemical Effects (SE) in the Remote Functionalization of C−X Bonds (X = H, C, Si) by Gaseous Metal Cations

substrate/M^+	process	KIE	SE
3-methylpentan-2-one/Fe^+	4,5-dehydrogenation[452]	2.1	1.5
2-methylbutyric acid/Fe^+	3,4-dehydrogenation[457]	1.8	1.6
3-methylvaleramide/Fe^+	4,5-dehydrogenation[458]	2.3	2.0
6-methyloctanenitrile/Co^+	ω-C−C-cleavage[470]	1.4	1.7
7-methylnonanenitrile/Co^+	ω-C−C-cleavage[470]	1.3	1.6
5-methyl-7-silylheptanenitrile/Mn^+	6,7-dehydrogenation[471]	2.2	2.1
5-methyl-7-silylheptanenitrile/Fe^+	6,7-dehydrogenation[471]	2.4	1.5
6-methyl-8-silyloctanenitrile/Mn^+	7,8-dehydrogenation[471]	2.2	1.9
6-methyl-8-silyloctanenitrile/Fe^+	7,8-dehydrogenation[471]	2.1	1.4
5-methyl-7-silylheptanenitrile/Co^+	6,7-dehydrosilylation[471]	1.6	4.1
6-methyl-8-silyloctanenitrile/Co^+	7,8-dehydrosilylation[471]	1.5	3.0

Table 13. Gaseous Transition-Metal Cluster Ions Which Either Activate Methane or Whose Selectivities in Alkane Activation Have Been Addressed in More Detail[a]

$[M]^{-/0/+}$	substrate	process(es)	method	comments	year
Fe_n^+	CH_4	C−H	GIB	$n = 2-15$	2001[485]
Co_n^+	CH_4	C−H	GIB	$n = 2-16$	2009[486]
Ni_n^+	CH_4	C−H	GIB	$n = 2-16$	2004[487]
Pt_n^-	CH_4	C−H	ICR	$n = 2-20$	2006[9a,181]
Pt_n	CH_4	C−H	various	$n = 1-4$	1991[182b]
Pt_n^+	CH_4	C−H	other	$n = 2-22$	2000[9]
Au_n^+	CH_4	association	ion trap	$n = 3, 5$	2009[488]
$Rh_mAr_n^+$	CH_4	C−H	ICR	$m = 2, 3$	1997[489]
$Pt_nCH_2^+$	CH_4	C−H	ICR	$n = 2-5$	2000[9d]
$V_3O_7^+$	C_3H_6, C_4H_8	C−H	GIB + theory		2006[59c]
$V_4O_{10}^+$	CH_4	C−H	GIB + theory		2006[59d]
$Fe_2O_2^+$	C_1-C_4 alkanes	C−H, C−C	ICR	CH_4, C_2H_6: n.r.	2001[490]
$Ni_2O_2^+$	C_1-C_4 alkanes	C−H	ICR	CH_4: n.r.	2005[491]
$Zr_mO_n^\mp$	CH_4, C_2H_6	n.r.	GIB	C_2H_2, C_2H_4	2008[246b,492]
$Nb_mO_n^\mp$	C_4H_{10}	C−H, C−C	GIB	anions inert	2001[493]
$Mo_mO_n^-$	CH_4	C−H	others + theory	hyperthermal	2006[494]
$Ta_mO_n^\mp$	C_4H_{10}	C−H, C−C	GIB	anions inert	2001[493]

[a] For abbreviations, see footnotes to Table 3.

which excludes any monitoring of selective processes. The cationic cluster Rh_{11}^+, for example, can completely dehydrogenate propane to afford the corresponding carbide cluster $Rh_{11}C_3^+$.[478] As far as the role of the charge is concerned, Berg et al. found that for $Nb_n^\pm$ as well as $Rh_n^\pm$ cluster ions the size matters much more than the actual charge state in C−H bond activation of benzene.[479,480] Like for the mononuclear species, in addition to the bare metals, the metal-oxide clusters received particular attention with respect to reactivity studies due to their direct relevance for oxidation catalysis.[481,482] The occurrence of C−H- and C−C-bond activations has in fact been reported in the reactions of $M_mO_n^+$ cations with ethane (M = V, Nb, Ta) as well as *n*-butane (M = Nb, Ta), whereas the corresponding anionic clusters $M_mO_n^-$ are unreactive.[483,484] For both bare metal clusters and their oxides, the experimental information about selectivity is very limited in most cases, however; unless detailed insight in this respect has been obtained, we therefore restrict the selection in Table 13 mostly to the activation of methane.

Compared to mononuclear species, fewer metal clusters react with methane, but up to now, several examples have been reported (Table 13). Most interesting is the case of platinum, which can activate methane to afford the corresponding carbene complexes in all charge states investigated, e.g. the Pt_n^- anions, the neutral Pt_n^- cluster, and Pt_n^+ cations. The gross rate constants for the anionic and cationic species are similar with a pronounced discontinuity for $n = 4$.[9a] As far as metal-oxide cluster ions are concerned, the first example for methane activation was found only in 2006 with the liberation of a $CH_3^\bullet$ radical in the reaction of bare $V_4O_{10}^+$ with methane.[59d] The low kinetic isotope effect observed experimentally and complementary dynamical calculations reveal that the C−H bond activation of methane by $V_4O_{10}^+$ occurs as a barrierless H-atom abstraction. Occurrence of this particular situation has been attributed to the localization of the spin in the open-shell, $3d^0$ compound $V_4O_{10}^+$ on one of the oxygen atoms, leading to an oxygen-centered radical. Based on this conception, with the $Al_{2n}O_{3n}^+$ cations ($n = 3-5$), more recently the first main-group metal-oxide clusters able to activate methane have been discovered.[366] In close analogy, also the metal-free oxide cluster $P_4O_{10}^+$ has been shown to activate methane.[495]

With respect to selectivity in hydrocarbon oxidations by metal-cluster ions, we take the Ag_2O^+ cation as an example, because it represents a triatomic model system for a megaton industrial process: the epoxidation of ethylene on silver contact. The desired product corresponds to ethylene oxide, but the first oxidation step can lead also to a byproduct, acetaldehyde, which is even thermodynamically favored. Acetaldehyde is easily further oxidized and finally ends up in combustion. Obviously, it would be of great importance if this parasite channel could be further suppressed or even eliminated. In order to steer the reaction conditions toward a larger selectivity for the formation of ethylene oxide, a deeper understanding of the reaction mechanism is necessary. The triatomic cation Ag_2O^+ is indeed capable of reproducing the key phenomena of the reaction with ethylene, as observed in the condensed phase.[412] The reaction starts with a coordination of the ethylene molecule to the silver atom of the Ag_2O^+ cation (Figure 18). It has to be noted that Ag_2O^+ carries an unpaired electron, which is localized at the central oxygen atom, and this situation remains unchanged also after

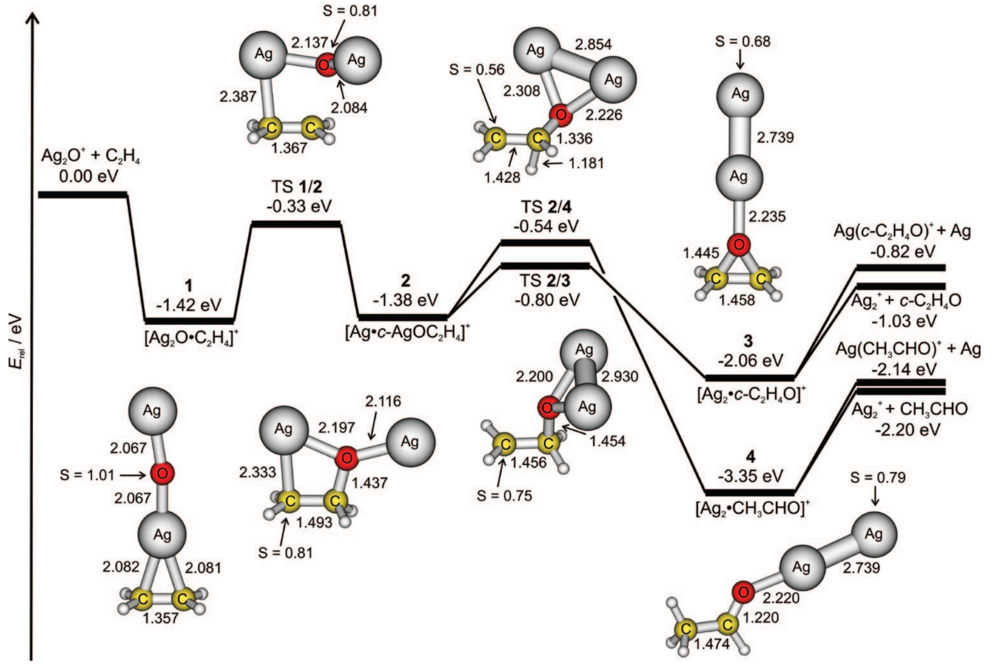


Figure 18. Potential-energy surface for O-atom transfer from Ag_2O^+ to ethylene, affording either ethylene oxide or acetaldehyde (relative energies in electronvolts and selected bond lengths in angstroms) calculated at the B3LYP/SDD:6-311+G(2d,p) level of theory. Further, computed spin densities are given for those atoms at which most of it is located. Reproduced from ref 412.

the coordination of ethylene. In the second step, the unsaturated oxygen atom attacks a carbon atom, which leads to a metallaoxetane intermediate in which the radical site is localized on one of the carbon atoms. This carbon-centered radical binds to the oxygen atom in the following step, which leads to the formation of the desired ethylene oxide coordinated to Ag_2^+. Alternatively, the C-centered radical can grasp a hydrogen atom from the neighboring methylene group, which results in the formation of acetaldehyde coordinated to Ag_2^+, and it thus represents the undesired mode of reactivity toward combustion. The selectivity in the oxidation of ethylene is thus given by the difference of energy barriers for the rearrangement of the metallaoxetane intermediate to the ethylene oxide or acetaldehyde complexes, respectively. The undesired hydrogen rearrangement is associated with a larger barrier and is therefore kinetically disfavored compared to the formation of ethylene oxide. The common metallaoxetane intermediate was also suggested for the condensed phase,[496] and therefore, it can be expected that a similar competition determines the ratio between ethylene oxide and combustion.

Finally, we note an example for remote functionalization of monofunctionalized alkanes by metal-cluster ions. Homo- and heterometallic dinuclear MM'^+ cluster (M, M′ = Fe, Co, Ni, Cu) cations generated by laser ionization of appropriate alloys react with alkylnitriles via functionalization of remote C−H bonds. However, the selectivities of the bond-activation processes taking place are partially masked by H/D exchange processes occurring in parallel.[497]

8. Conclusions and Outlook

Motivated by the landmark paper of Allison, Freas, and Ridge in 1979 about the first example of gas-phase C−H bond activation of alkanes by bare transition-metal ions,[26a] extensive research efforts have been devoted to this topic. The scope of these studies very closely reflects the actual developments in the field itself and in science and technology in general. Thus, the earlier experimental studies were mostly restricted to atomic cations of 3d transition metals, while the new ionization methods introduced about 1990 (laser desorption, Smalley-type cluster sources, electrospray ionization) opened horizons not only to the entire periodic system but also to homo- and heterometallic clusters, their oxides, etc., and also rather complex metal complexes directly transferred from solution to the gas phase via electrospray ionization.[54] Further, due to significant technological improvements on the one hand and seminal studies of the laboratory of P. B. Armentrout on the other,[31] reactivity studies based on multipole analyzers by and large replaced sector-mass spectrometry (not only in this area). In the context of metal-ion chemistry, the key advantage of guided ion beam studies using multipole analyzers is that not only the thermal reactivity but also the energy dependences of the various channels can be accessed fast and accurately. The major breakthrough, however, certainly came from theory. Up to the mid 1990s, the calculation of a complete potential-energy surface for a given reaction of a coordinatively unsaturated, open-shell transition-metal species represented a major challenge and was generally not attempted. Density functional theory came in fact like an invasion because it allowed the investigation of entire reaction pathways in reasonably short time, and—while certainly not ultimately precise—the results are accurate enough to derive useful mechanistic consequences. In fact, nowadays DFT calculations even pose challenges to experimentalists by predicting particularly reactive metal cations which have not been generated so far.[408]

Irrespective of the specific knowledge achieved for a large variety of reactions, the studies summarized in this work have provided a comprehensive picture about the necessities for C−H bond activation by isolated metal species (e.g., electron configuration, charge and valence states, etc.) which not only is useful in this particular area of specialization, but also has implications for different fields of research. Similarly, the very rich thermochemical database for gaseous transition-metal compounds which has been established in the course of these studies provides a solid foundation for future research.[31,60a,498] These values not only allow prediction of—at least partially—the shapes of potential-energy surfaces and extrapolation from one element to its heavier homologues in the periodic table, but also comparisons along the transition metals within a *n*d series and between metal complexes bearing different types of ligands.

In the specific context of alkane activation, the number of examples studied so far is huge, and the results show a large variation. Nevertheless, some general trends can be extracted from the data presented here. (i) The activation of alkanes is most efficient for cationic reagents, as these are strong electrophiles which can favorably interact with the otherwise quasi "inert" alkanes. Not at all surprisingly, the few metal dications studied so far can be regarded as superelectrophiles[499] and thus efficiently activate alkanes.[199] (ii) The ability of many bare metal ions (and their clusters) to activate alkanes is rapidly quenched upon ligation, with the consequence that the primary products often do not undergo any subsequent reactions. In a more general sense, this implies that the bond activations seen for these types of model species in the gas phase are likely to be suppressed at higher coverage or pressures of reactants and/or products. (iii) For metal oxides, a pronounced reactivity of the cationic species is clearly apparent from the data achieved so far. However, a sufficiently large electrophilicity of the metal-oxo species is only a requisite condition for alkane activation, which does not suffice alone. The major additional requirement is at least some character of an oxygen-centered radical in the metal-oxo species, which significantly lowers the barriers associated with H-atom abstraction—often the rate-determining step.

Obviously, many open questions are still left. Not only could some of the presumably most reactive metal-oxide cations, e.g. CuO^+, not have been made so far in quantities sufficient for subsequent reactivity studies, but also almost the entire area of metal halides still poses several challenges to be addressed in the future. Likewise, several organometallic ions are of particular interest with respect to the vastly developing field of new C−C coupling reactions.[500] In the context of the time-honored Ullmann reaction,[501] for example, the fate of Cu−C intermediates would be of high interest, and similar arguments apply for the manifold of Pd-mediated C−C couplings, and most recently also iron shows remarkable performance in this respect.

At the end, we would like to address a more general aspect of scientific research. In addition to the rich mechanistic as well as methodological knowledge collected in the course of the mostly mass spectrometric work summarized in this review, three key concepts have been derived from the gas-phase studies which had and still have impact also on other areas of sciences.

- The *remote functionalization* of monofunctional alkanes by bare metal ions has provided a conceptually new approach for the activation of C−H, C−C, and C−Si bonds which offers interesting perspectives for stereoselective processes and also has implications for biochemical transformations. The simplicity of the approach and the often high selectivities achieved render the gas-phase protocol a very attractive variant for the functionalization of nonactivated C−H bonds. A key aspect of future work would be to provide a sufficient thermochemical driving force by inclusion of an oxidation step (e.g., remote functionalization by MO^+ rather than M^+ ions).
- The relevance of *multicentered transition structures* in the reactions of late transition-metal ions demonstrates that the classical concepts of organometallic chemistry derived from "stationary" approaches, e.g. NMR or X-ray characterization of intermediates, cannot be simply transferred between different metals. Even if, for example, a certain dihydrido intermediate has unambiguously been characterized in the case of titanium, the analogue species might not even be a minimum in the case of iron, cobalt, or nickel. Conclusions based on "horizontal" comparisons among the d-elements should thus be taken with care, even when an equal d-electron count is ensured.
- The concept of *two-state reactivity*, originating from a close collaboration of experimentalists and theoreticians aimed to rationalize the "four-atom reaction" of $FeO^+ + H_2$,[297] meanwhile developed to a reactivity paradigm with rather general relevance in chemical sciences and particularly also biology. The wide impact of this "gas-phase result" is also manifested in the origin of the citations of the associated feature article,[248a] which mostly are from other areas of specializations than those of its authors (theory and mass spectrometry) and cover various areas of research such as catalysis, fundamental physics, biochemical processes, and even medical aspects.

In summary, many aspects of the metal-mediated activation of hydrocarbons in the gas phase have been addressed already in the past, but even more challenges emerge for the future. Particular tasks concern selective partial oxidation reactions because their facile realization, e.g. the reaction $CH_4 + {}^1/_2O_2 \rightarrow CH_3OH$ at room temperature and moderate pressure, might in fact significantly contribute to the severe problems of global energy management and resources mankind faces in this century. In this respect, two key aspects may be summarized as follows.[502] (i) How can overoxidation of methane be prevented? Or, in a more general sense, how can a reagent be designed that reacts more efficiently with an alkane than with an alcohol? (ii) Does there exist a general solution to the spin- and stoichiometry problems imposed by the use of molecular oxygen, having a triplet ground state, as the terminal oxidant? Both last points formulate sufficiently challenging tasks for future research such that fundamental studies of alkane activation by isolated metal species will remain a fruitful and inspiring playground for both experimentalists and theoreticians with fundamental insight as well as stimuli for applied research as deliverables.

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