C–H Activation

DOI: 10.1002/anie.200600188

Thermal Activation of Methane by Tetranuclear $[V_4O_{10}]^+$**

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Dedicated to Professor Ernst-Ludwig Winnacker on the occasion of his 65th birthday

Selective activation of C–H bonds and functionalization of hydrocarbons, in particular of methane, have been referred to as one of the "holy grails" in chemistry.[1] A number of factors make the activation of saturated hydrocarbons quite difficult, for example, the significant energies required for both heterolytic and homolytic bond cleavage, negligibly small (if not negative) electron affinities, large ionization energies, huge HOMO/LUMO gaps, and the extremely high pK_a values of the organic substrates.[2] However, in the past two decades researchers have found that transition-metal complexes can be used to surmount some of these obstacles [1b,2,3] to the extent that "with detailed knowledge of the underlying reaction mechanisms, the rational design of C–H activation and functionalization systems can become a realistic goal instead of a 'holy grail'."[4] Nevertheless, the large-scale use of, for example, methane as a chemical feedstock and its selective functionalization by affordable and environmentally benign reagents, avoiding harsh and expensive reaction conditions,[5a,b] is still limited by currently available technol-

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[**] Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (SFB 546) is acknowledged. S.F. was supported by a GRK352 fellowship.

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ogy, and economically competitive and attractive processes have yet to be developed.[5a,d]

Greater progress has been made in understanding the elementary steps involved in these reactions.[1b] Detailed insight has been obtained into the particular role of electronic structures of transition metals in C–H bond activation, and mechanistic aspects have been studied in well-designed gas-phase experiments using advanced mass-spectrometric techniques in conjunction with theoretical studies,[6] in which relativistic effects were demonstrated to be crucial.[7]

These effects, which may also explain the unique role platinum ions play in the Shilov and related systems,[3c] are also responsible for the different behavior of 5d versus 3d transition-metal oxides. For example, $[PtO]^+$ reacts with CH_4 at the collisional limit (reaction efficiency, $\phi = 1$) to yield the carbene complex $[Pt(CH_2)]^+$ and H_2O as the predominant products,[8] whereas the isoelectronic $[NiO]^+$ reacts five times more slowly and gives rise to Ni^+ and CH_3OH only.[9] Similarly, $[FeO]^+$ oxygenates methane,[9] while its third-row congener $[OsO]^+$ ($\phi = 0.6$) exclusively dehydrogenates methane to yield $[Os(O)CH_2]^+$.[10] With regard to the role of formal oxidation states of $[MO_n]^+$ ions ($n = 1$–3), Kretzschmar et al. discovered a strong dependence on the number of oxygen atoms: Whereas the bare metal cation Mo^+ and the lower valent oxides $[MoO_n]^+$ ($n = 1, 2$) do not react at all with CH_4, the radical cation $[MoO_3]^+$ promotes homolytic C–H bond activation [Eq. (1)].[11] Similar results were reported by Irikura and Beauchamp for gas-phase reactions of $[OsO_n]^+$ ($n = 0$–4) with CH_4,[10] [Eq. (2)–(6)].

$$CH_4 + [MoO_3]^+ \rightarrow [MoO_2(OH)]^+ + CH_3 \quad (1)$$

$$CH_4 + Os^+ \xrightarrow{\phi=0.3} [Os(CH_2)]^+ + H_2 \quad (2)$$

$$CH_4 + [OsO]^+ \xrightarrow{\phi=0.6} [Os(O)CH_2]^+ + H_2 \quad (3)$$

$$CH_4 + [OsO_2]^+ \xrightarrow{\phi=0.5} [Os(O)CH_2]^+ + H_2O \quad (4)$$

$$CH_4 + [OsO_3]^+ \not\rightarrow \quad (5)$$

$$CH_4 + [OsO_4]^+ \xrightarrow{\phi=0.7} [OsO_3(OH)]^+ + CH_3 \quad (6)$$

Clearly, the driving force in the osmium reactions [Eq. (2)–(4)] is the tremendous energy of the Os^+–CH_2 bond. In contrast to $[MoO_3]^+$,[11] $[ReO_3]^+$,[10] and $[OsO_4]^+$, $[OsO_3]^+$ is not capable of methane activation. Undoubtedly, in reactions with CH_4 the particular electronic structures of $[MO_n]^+$ are important;[6d,7b,12] in a different context[6e] the cluster size of the transition-metal oxides was proposed to play a role. In this communication we focus on the latter aspect.

Here, we will describe the reactivity of vanadium oxide cluster cations as a prototypical example for early 3d transition-metal oxides. Not unexpectedly, owing to their large M^+–O bond energies,[12] practically none of the diatomic 3d early-transition-metal oxides react with CH_4 under thermal conditions or at best only sluggishly.[13] As will be demonstrated, this finding cannot be extrapolated to polynuclear oxide clusters, which have been suggested to be more appropriate models for surface-mediated hydrocarbon bond-activation processes.[9,14]

We performed out experiments with a quadrupole-based mass spectrometer equipped with an electrospray ionization (ESI) source. The latter is used to generate various di-, tri, and tetranuclear vanadium oxide ions of the general formula $[V_mO_nH_o]^+$ ($m = 1$–4, $n = 1$–11, $o = 0$–1).[15] Of the numerous mass-selected vanadium oxide and hydroxide cations investigated, only the d^0 radical cation $[V_4O_{10}]^+$ reacts spontaneously with methane [Eq. (7)], resulting in the abstraction of

$$[V_4O_{10}]^+ + CH_4 \rightarrow [V_4O_{10}H]^+ + CH_3 \quad (7)$$

one hydrogen atom to produce the hydroxide cluster oxide $[V_4O_9(OH)]^+$ and a neutral methyl radical (Figure 1a). Like-

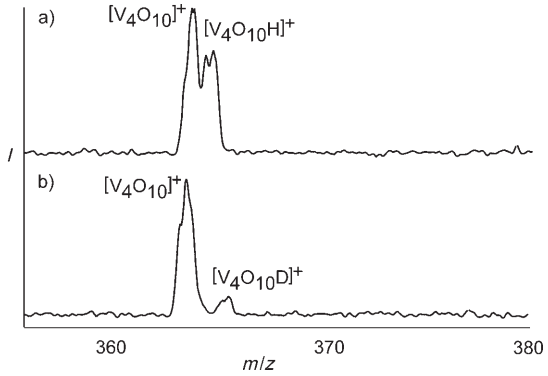

Figure 1. Reaction of mass-selected $[V_4O_{10}]^+$ with a) CH_4 and b) CD_4.

wise, labeling experiments using CD_4 (Figure 1b) yielded $[V_4O_9(OD)]^+$ and CD_3. Further, an intramolecular kinetic isotope effect (KIE) of 1.35 ± 0.28 can be derived from the ratio of the products $[V_4O_{10}H]^+$ and $[V_4O_{10}D]^+$ from the reaction of $[V_4O_{10}]^+$ with CH_2D_2. A slightly larger KIE of 2.0 was reported for the $[MoO_3]^+/CH_2D_2$ system,[11] thus pointing to a common bond-activation mechanism. In the multipole set-up used for the present experiments, absolute rate constants (k_r) for the reactions cannot be determined directly. Therefore, we used the well-studied reaction of bare Pt^+ with methane as a reference to convert the relative rate constant k_{rel} into absolute values. We found $k_r(V_4O_{10}^+) = (5.5 \pm 0.69) \times 10^{-10}\ cm^3\,s^{-1}$ ($\phi = 0.6$).[8a,16]

Further, we attempted to enter the potential energy surface of the reaction from a different entry by reacting mass-selected $[V_4O_9]^+$ with neutral methanol. The channel affording $[V_4O_{10}H]^+ + CH_3$ is also observed here, although it is a minor contributor [$< 3\%$; Eq. (8)]. The predominant

$$[V_4O_9]^+ + CH_3OH \rightarrow [V_4O_{10}H]^+ + CH_3 \quad (8)$$

reaction was molecular addition to generate $[V_4O_9(CH_3OH)]^+$ (38%). Other reactions include oxygen transfer to form $[V_4O_8]^+$ possibly with concomitant formation of $CH_2O + H_2O$ (12%), elimination of formaldehyde to form $[V_4O_9H_2]^+$ (9%), liberation of dihydrogen to generate $[V_4O_9(CH_2O)]^+$ (8%), elimination of water to produce $[V_4O_9CH_2]^+$ (21%), addition of methane concomitant with loss of one oxygen atom (9%), and formation of $[V_4O_{10}H]^+$ concomitant with generation of CH_3 (3%). The occurrence of reaction (7)

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implies that the bond energy of the newly formed O–H bond in the ionic cluster exceeds the C–H bond energy of methane (439 kJ mol^{-1});[17] further, OH abstraction from methanol in reaction (8) implies a lower limit of 367 kJ mol^{-1} for the strength of the V–(OH) bond in the $[V_4O_{10}H]^+$ cluster.[18]

As insight into the mechanistic details of the C–H bond-activation step is difficult to obtain by experimental means, computational studies were carried out. According to B3LYP calculations, the most stable isomer of the $[V_4O_{10}]^+$ ion has a slightly distorted tetrahedral cage structure with C_s symmetry. This structure was previously predicted to be the most stable isomer among many different structures for neutral V_4O_{10}[19] and confirmed by IR spectroscopy for the corresponding anion, $[V_4O_{10}]^-$.[20] In the radical cation $[V_4O_{10}]^+$ one valance electron is missing from one V=O bond, leading to an elongation of the vanadyl bond (see Figure 2). The spin density has the shape of a p orbital and is mainly localized at the vanadyl oxygen atom. A small amount of the spin density is also delocalized over the two closest framework oxygen atoms.

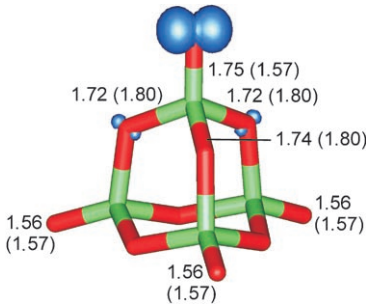

Figure 2. Structure of the most stable isomer of $[V_4O_{10}]^+$ with spin density (blue areas). V–O distances for $[V_4O_{10}]^+$ and V_4O_{10} (in parentheses) are given in Å.

The coordination of methane to the cluster and smooth hydrogen-atom abstraction is associated with a remarkably large gain of energy, 122 kJ mol^{-1} (Figure 3). It has to be noted no encounter complexes of the type $[V_4O_{10}]^+ \cdot CH_4$ were found

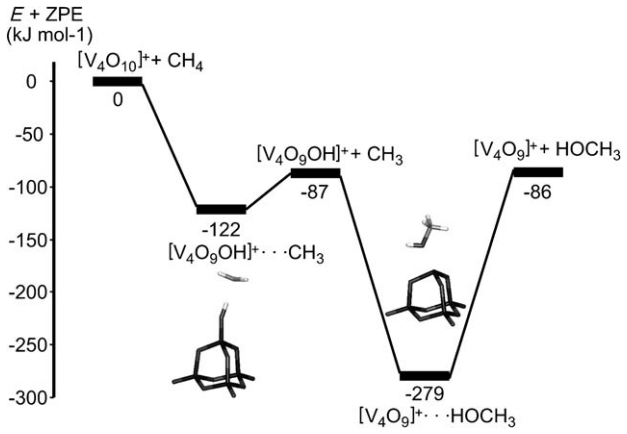

Figure 3. Energy diagram for the reaction of $[V_4O_{10}]^+$ and methane. The values are relative to the entrance channel, corrected for zero-point energy, and given in kJ mol^{-1}.

in the structure optimizations, suggesting that the reaction proceeds without a noticeable reaction barrier by direct H-atom abstraction to form the intermediate $[V_4O_{10}H]^+ \cdot CH_3$. In the latter, the methyl group is very loosely coordinated to the hydrogen atom of the newly formed, metal-bound hydroxy group (C–H distance: 1.819 Å), and the reaction is completed by loss of a methyl radical concomitant with formation of $[V_4O_{10}H]^+$ as the ionic product. The computed reaction exothermicity of 87 kJ mol^{-1} and the absence of barriers are in full accordance with the experimentally observed occurrence of the ion–molecule reaction under thermal conditions. According to the calculations, the reaction of $[V_4O_9]^+$ with methanol yields a very stable addition complex with an interaction energy of −193 kJ mol^{-1}. This high energy gain is attributed to solvation of the unfavorable threefold-coordinated vanadium atom in $[V_4O_9]^+$. The energy of separated $[V_4O_9OH]^+ + CH_3$ is virtually equal to the entrance channel energy of separated $[V_4O_9]^+ + HOCH_3$; thus loss of a methyl radical can hardly compete with the other observed reaction channels, and it is expected that $[V_4O_9]^+ + HOCH_3$ yields $[V_4O_9OH]^+$ merely as a marginal product, in agreement with the experimental findings.

To clarify whether reaction (7) is indeed barrierless, molecular dynamics (MD) simulation was performed (Figure 4). The starting point is an optimized structure of

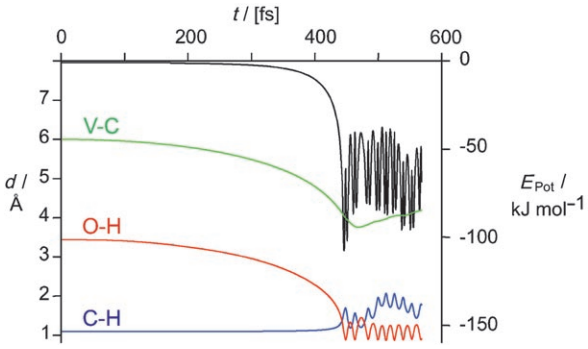

Figure 4. Evolution of the potential energy and bond lengths in the MD simulation of the reaction of $[V_4O_{10}]^+$ and methane. The energy is shown in black, d(C–H) in blue, d(O–H) in red, and d(V–C) in green. The fluctuations after 450 fs result from vibrational motions, mainly of the OH group.

$[V_4O_{10}]^+$ and CH_4 in which the V–C distance is constrained to 6 Å to prevent the methane from reacting with the cluster. The simulation is started with zero initial velocities when this constraint is lifted. Thus the reaction is driven only by the small attractive forces between methane and the cluster; vibrational and rotational energies are nonexistent. For the first 450 fs of the simulation the potential energy decreases steadily, indicating a barrierless process. In parallel the O–H and V–C distances decrease and the C–H distance increases, indicating the progress of the reaction. After 450 fs when the system contains 102 kJ mol^{-1} of kinetic energy, energy is transferred into CH and OH stretching vibrations, corresponding to an oscillation of the hydrogen atom between the vanadyl O atom and the methyl C atom. This is evident as fluctuations of the potential energy. The plot in Figure 4 also

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shows the V–C distance, which decreases up until $t = 470$ fs and then slowly increases. This indicates the beginning of the expulsion of the CH_3 radical, which would be completed only after significantly longer simulation times.

The progression of the reaction can also be seen by inspection of the spin densities shown in Figure 5. In the initial state (structure a in Figure 5), the spin density is similar to that of the isolated $[V_4O_{10}]^+$ ion (Figure 2) and only slightly more delocalized. Structure b was obtained from MD simulation after 443 fs. The O–H and C–H distances are almost identical, and the spin density is distributed between the vanadyl oxygen and the carbon atoms and polarized along the O-H-C axis. Finally, in product c the spin density is completely transferred to the methyl radical, and the shape is again p-orbital-like with only slight distortion towards the newly formed OH group. One explanation of the lack of energy barriers in this reaction is that $[V_4O_{10}]^+$ is highly reactive owing to its radical-cation nature.[21]

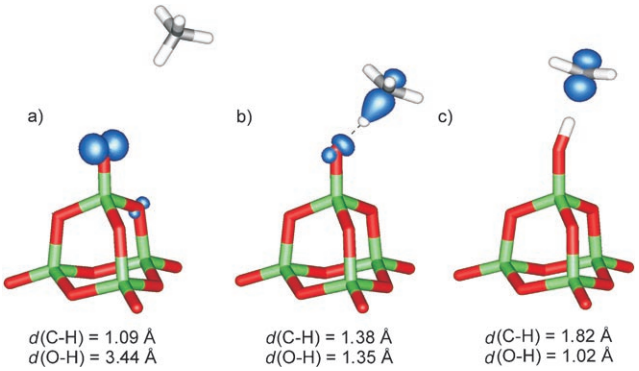

Figure 5. Spin density for the reaction of $[V_4O_{10}]^+$ and methane after a) 0 fs and b) 443 fs. c) Spin density of the optimized product structure. C–H and O–H distances are given below the structures.

Our combined experimental and theoretical studies provide the first example for the thermal activation of methane by a polynuclear transition-metal oxide. This observation is not trivial, for it had been noted earlier[9,14a] that the often extremely reactive mononuclear metal oxides[12] are not ideal model systems relevant for an understanding of a real-life oxidation catalyst; larger systems, that is, cluster oxides, are better suited to serve this purpose.

Experimental Section

The experiments were carried out using a tandem mass spectrometer with QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization (ESI) source as described elsewhere.[22] Briefly, vanadium oxide clusters were generated by ESI of a solution of $V_6O_7(OCH_3)_{12}$ in CD_3OD. Then, $V_4O_{10}^+$ was mass-selected using Q1 and reacted with methane in the hexapole at pressures on the order of 10^{-4} mbar, which approximately corresponds to single-collision conditions. The reaction was followed by detection of the ionic products using Q2. Ion-reactivity studies were performed at an interaction energy in the hexapole (E_{lab}) nominally set to 0 eV.[15,23]

Calculations were performed using the hybrid density functional theory method B3LYP[24] with triple-ζ plus polarization basis sets (TZVP)[25] employing Turbomole 5.7.[26] B3LYP has been shown previously to describe vanadium oxides in good agreement with available experimental data and the results of quantum chemical methods that explicitly include electron correlation.[27] MD simulation was performed with zero initial velocities from an optimized structure with a fixed distance between the vanadium and carbon atoms.

Received: January 17, 2006
Published online: May 26, 2006

Keywords: C–H activation · density functional calculation · mass spectrometry · molecular dynamics · vanadium oxides

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[21] More generally speaking, the fact that $[V_4O_{10}]^+$ [Eq. (7)], $[MoO_3]^+$ [Eq. (1)], and $[OsO_4]^+$ [Eq. (6)] bring about homolytic C–H activation of CH_4 while $[OsO_3]^+$ does not [Eq. (5)] underlines the particular role of the radical character of oxygen in this reaction. This conjecture is further supported by the notion that Li-doped MgO, which contains an $O^{\bullet-}$ radical anion, is also predicted to bring about methane activation: a) D. J. Driscoll, W. Martir, J.-X. Wang, J. H. Lunsford, *J. Am. Chem. Soc.* **1985**, *107*, 58; b) S. J. Korf, J. A. Roos, N. A. De Bruijn, J. G. Van Ommen, J. R. H. Ross, *Catal. Today* **1988**, *2*, 535–545; c) S. J. Korf, J. A. Roos, N. A. De Bruijn, J. G. Van Ommen, J. R. H. Ross, *Appl. Catal.* **1990**, *58*, 131–146; d) V. R. Choudhary, S. T. Chaudhari, M. Y. Pandit, *J. Chem. Soc. Chem. Commun.* **1991**, 1158–1159; e) R. Orlando, F. Cora, R. Millini, G. Perego, R. Dovesi, *J. Chem. Phys.* **1996**, *105*, 8937–8943; f) C. R. A. Catlow, S. A. French, A. A. Sokol, J. M. Thomas, *Philos. Trans. R. Soc. London Ser. A* **2005**, *363*, 913–936.
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