

C–H Activation

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Gas-Phase Oxidation of Propane and 1-Butene with $[\text{V}_3\text{O}_7]^+$: Experiment and Theory in Concert***Sandra Feyel, Detlef Schröder, Xavier Rozanska, Joachim Sauer,* and Helmut Schwarz***Dedicated to Professor Siegfried Blechert on the occasion of his 60th birthday*

Vanadium oxides are employed as efficient oxidation catalysts in various processes such as the oxidative dehydrogenation of propane and the formation of maleic anhydride from butane.^[1] Nevertheless, mechanistic details of the surface reactions, in particular of the initial C–H activation remain to be elucidated. To obtain more information about intrinsic structure–reactivity correlations of vanadium oxides, a number of vanadium oxide ions have been studied in the gas phase both theoretically^[2–4] and experimentally.^[5–13] Here, we report experimental results on the oxidation of propane and 1-butene by mass-selected $[\text{V}_3\text{O}_7]^+$, corroborated by quantum chemical calculations using density functional theory (DFT). The cation $[\text{V}_3\text{O}_7]^+$ was chosen because it represents the smallest polynuclear V/O cluster cation containing only formal V^{V} .^[2b,3c] In addition to propane, 1-butene was selected as a representative of a small hydrocarbon that binds more strongly with $[\text{V}_3\text{O}_7]^+$. In general, oxidative

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dehydrogenation (ODH) of hydrocarbons involves reduction of the metal center ($[\text{V}_3\text{O}_7]^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow [\text{V}_3\text{O}_7\text{H}_2]^+$). This is brought about by transfer of two hydrogen atoms (or equivalently, two protons and two electrons), thus resulting in the dehydrogenation of propane to give propene ($\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + 2\text{H}$) and of 1-butene to butadiene ($\text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_6 + 2\text{H}$). In a mass spectrometric experiment, two alternative product channels could indicate ODH. Either propene and butadiene are lost as neutrals concomitant with two hydrogen atoms being transferred to $[\text{V}_3\text{O}_7]^+$ to form $[\text{V}_3\text{O}_7\text{H}_2]^+$, or neutral water may be eliminated while the dehydrogenated hydrocarbon remains bound at the metal oxide cation to yield $[\text{V}_3\text{O}_6(\text{C}_3\text{H}_6)]^+$ and $[\text{V}_3\text{O}_6(\text{C}_4\text{H}_6)]^+$, respectively.

The experimental investigation of the $[\text{V}_3\text{O}_7]^+$ /hydrocarbon systems uses a quadrupole-based mass spectrometer equipped with an electrospray-ionization source.^[14] Ion-molecule reactions (IMRs) of mass-selected $[\text{V}_3\text{O}_7]^+$ with propane formally result in molecular addition of the hydrocarbon to the vanadium oxide ion to form $[\text{V}_3\text{O}_7(\text{C}_3\text{H}_8)]^+$ (Figure 1a) and yields no products indicative for an ODH process. In contrast, oxidative dehydrogenation to yield $[\text{V}_3\text{O}_7\text{H}_2]^+$ concomitant with formation of neutral butadiene is indeed observed in the reaction of mass-selected $[\text{V}_3\text{O}_7]^+$ with 1-butene (Figure 1b, Table 1). In addition, four minor

Table 1: Experimentally observed, normalized intensities and relative reaction rates for various ion-molecule reactions relevant in the present context.

Reactants	Products ^[a]	k_{rel}
$[\text{V}_3\text{O}_7]^+ + \text{C}_3\text{H}_8 \rightarrow$	$[\text{V}_3\text{O}_7(\text{C}_3\text{H}_8)]^+$ (100)	0.03
$[\text{V}_3\text{O}_6]^+ + n\text{-C}_3\text{H}_7\text{OH} \rightarrow$	$[\text{V}_3\text{O}_7\text{H}_2]^+ + \text{C}_3\text{H}_6$ (75) $[\text{V}_3\text{O}_6(\text{C}_3\text{H}_7\text{OH})]^+$ (25)	1.00 ^[b,c]
$[\text{V}_3\text{O}_6]^+ + i\text{-C}_3\text{H}_7\text{C}(\text{OH})\text{HCH}_3 \rightarrow$	$[\text{V}_3\text{O}_7\text{H}_2]^+ + \text{C}_3\text{H}_6$ (82) $[\text{V}_3\text{O}_6(\text{C}_3\text{H}_7\text{OH})]^+$ (18)	0.63
$[\text{V}_3\text{O}_7\text{H}_2]^+ + \text{C}_3\text{H}_6 \rightarrow$	$[\text{V}_3\text{O}_7\text{H}_2(\text{C}_3\text{H}_6)]^+$ (100)	0.24
$[\text{V}_3\text{O}_7]^+ + \text{C}_4\text{H}_8 \rightarrow$	$[\text{V}_3\text{O}_7\text{H}_2]^+ + \text{C}_4\text{H}_6$ (64) ^[d] $[\text{V}_3\text{O}_7(\text{C}_2\text{H}_4)]^+ + \text{C}_2\text{H}_4$ (8) $[\text{V}_3\text{O}_7(\text{C}_4\text{H}_8)]^+$ (7) $[\text{C}_4\text{H}_8]^+ + [\text{V}_3\text{O}_7]$ (4) $[\text{C}_4\text{H}_7]^+ + [\text{V}_3\text{O}_7\text{H}]$ (17)	0.24

[a] Branching ratios in brackets. [b] Relative rates normalized to this reaction. [c] The reaction of bare Pt^+ with CH_4 was used as a reference to convert the relative rate constant (k_{rel}) into absolute values, which leads for the reaction of $[\text{V}_3\text{O}_6]^+$ with $\text{C}_3\text{H}_7\text{OH}$ to $k_r = (1.3 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.^[18] The collision rate constant amounts to $1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.^[19] [d] The primary ionic products rapidly add butene to yield $[\text{V}_3\text{O}_7\text{H}_2(\text{C}_4\text{H}_8)]^+$; see Figure 1b.

product channels are associated with C–C bond cleavage to lead to the corresponding $[\text{V}_3\text{O}_7(\text{C}_2\text{H}_4)]^+$ cation with parallel elimination of ethene, mere association to form $[\text{V}_3\text{O}_7(\text{C}_4\text{H}_8)]^+$, and electron as well as hydride transfers to yield purely organic cations and neutral vanadium species.^[14] For the oxidative dehydrogenation of 1-butene, labeling experiments demonstrate that the two hydrogen atoms transferred to $[\text{V}_3\text{O}_7]^+$ originate specifically from the C3 and C4 positions of 1-butene. We note in passing that the product ion $[\text{V}_3\text{O}_7\text{H}_2]^+$ displays a dihydroxide structure rather than that of a water complex, that is, $[\text{V}_3\text{O}_5(\text{OH})_2]^+$ rather than $[\text{V}_3\text{O}_6(\text{OH}_2)]^+$.

To understand why ODH is not observed when $[\text{V}_3\text{O}_7]^+$ reacts with propane, but occurs for 1-butene, we apply density functional theory (DFT). Calculations show that the reactivity difference can be traced back to the initial C–H activation step. It is not the aim of this communication to discuss the entire mechanism, which forms the subject of a separate computational full paper.^[15]

The reaction of propane with $[\text{V}_3\text{O}_7]^+$ starts with formation of the remarkably stable (-107 kJ mol^{-1}) ion-molecule complex **1** (Scheme 1, Figure 2). The secondary carbon atom of propane attaches to a vanadium site, and the $[\text{V}_3\text{O}_7]^+$ structure deforms such that one oxygen atom of the cluster changes its coordination from three- to twofold. The next step corresponds to a formal [2+2] addition of a secondary C–H bond onto the $\text{V}=\text{O}$ unit yielding intermediate **2** (-166 kJ mol^{-1}). These steps involve only closed-shell singlet species. The transition structure $\text{TS } \mathbf{1/2}$ lies 13 kJ mol^{-1} above the separated reactants. In the reaction of ethane and propane with the formal V^{V} compound $[\text{VO}_2]^+$, addition of C–H bonds across a $\text{V}=\text{O}$ unit has also been identified as an initial step, although in these systems the transition structures are below the respective entrance channels because $[\text{VO}_2]^+$ binds alkanes more strongly.^[12b,13a] In a thermal gas-phase reaction, $\text{TS } \mathbf{1/2}$ constitutes a bottleneck because dissociation of the

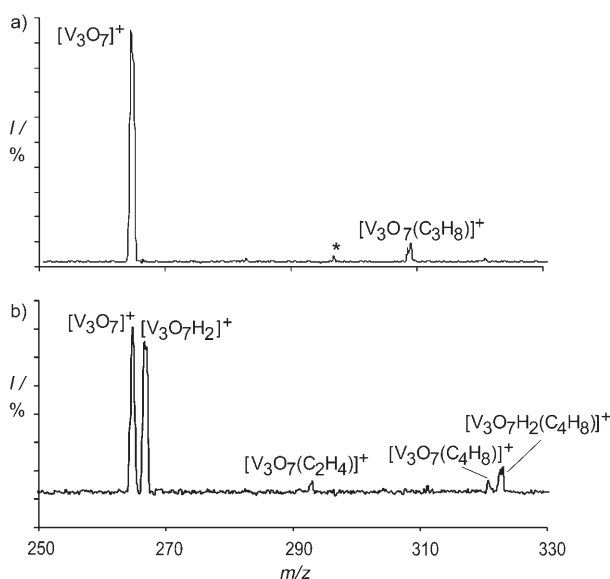
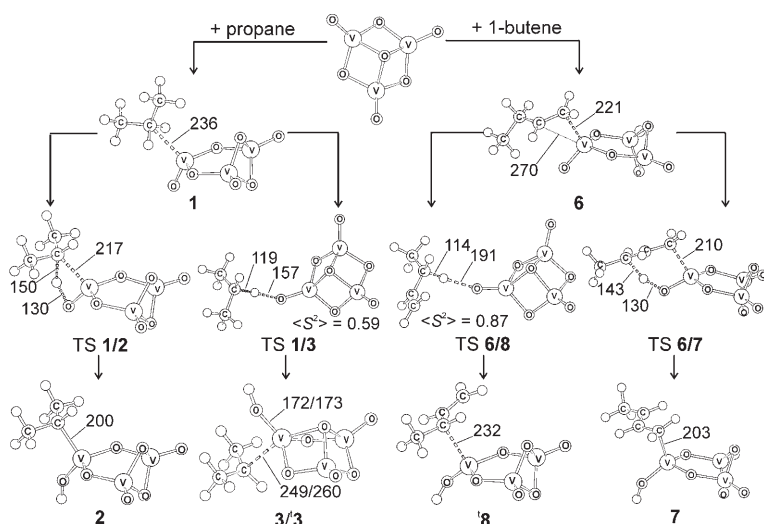


Figure 1. IMRs of $[\text{V}_3\text{O}_7]^+$ with a) propane and b) 1-butene. p (hydrocarbon) = 2.5×10^{-4} mbar. The signal denoted with an asterisk in Figure 1a is due to residual gases present in the hexapole.



Scheme 1. Reaction intermediates and transition structures in the oxidative dehydrogenation of propane and of 1-butene by $[\text{V}_3\text{O}_7]^+$. Selected distances are given in pm, and triplets are indicated by a superscript t. $\langle S^2 \rangle$: spin operator value (see the Experimental Section and the Supporting Information).

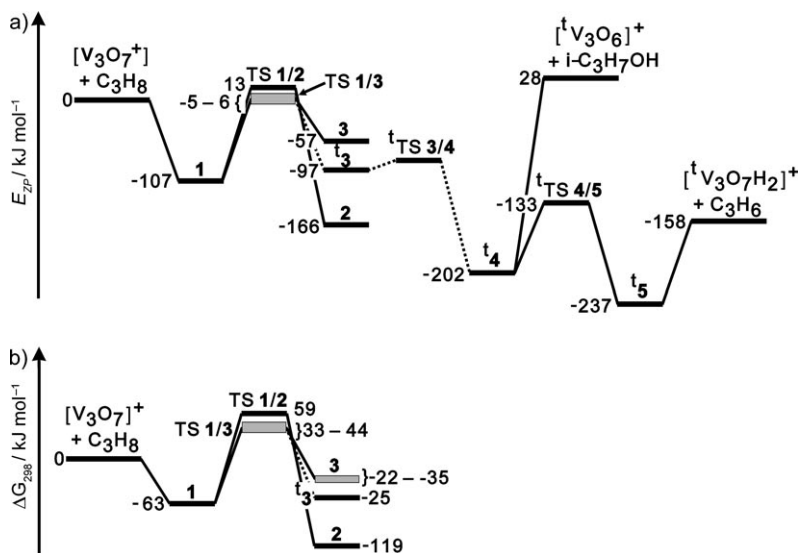


Figure 2. a) Relative energies (E_{zp} at 0 K) for the reaction pathways for oxidative dehydrogenation of propane by $[\text{V}_3\text{O}_7]^+$. The transition from $\mathbf{3}$ to $\mathbf{4}$ involves a complex rearrangement over several steps which will be described elsewhere.^[15] b) Free energies (ΔG_{298}) for the initial C–H activation steps. Triplets are indicated by a superscript t.

reactant complex $\mathbf{1}$ ($\Delta G_{298} = -63 \text{ kJ mol}^{-1}$) into the reactants ($\Delta G_{298} = 0 \text{ kJ mol}^{-1}$) is entropically favored compared to passage via TS1/2 ($\Delta G_{298} = 59 \text{ kJ mol}^{-1}$; see the Supporting Information).

Another conceivable mechanism commences by abstraction of a hydrogen atom from a secondary C–H bond by a V=O unit of $[\text{V}_3\text{O}_7]^+$. This requires decoupling of the electron pair in the C–H bond and proceeds via a biradicaloid TS1/3 to give the radical pair $[\text{V}_3\text{O}_7\text{H}^+\cdot\text{C}_3\text{H}_7\cdot]$ (structure $\mathbf{3}$ in Scheme 1). With the exception of an elongated V–C bond (249 instead of 200 pm), structure $\mathbf{3}$ is similar to $\mathbf{2}$. The existence of two minima along the V–C bond coordinate can

be attributed to an avoided crossing of the potential energy surface (PES) for the dissociation of the C–V σ bond into two σ radicals, $\text{C–V} \rightarrow \text{C}\cdot + \cdot\text{V}$, and that for formation of the $[\text{V}_3\text{O}_7\text{H}^+\cdot\text{C}_3\text{H}_7\cdot]$ pair from the separated radicals with the single electron on $[\text{V}_3\text{O}_7\text{H}]^{+\cdot}$ occupying a stable d orbital instead of a σ hybrid orbital, thus creating a $\text{V}^{\text{IV}}(\text{d}^1)$ site.

On the singlet PES, the energy barrier for this step is computed to be in the range of -5 to 6 kJ mol^{-1} relative to the entrance channel. The Gibbs free energy barrier amounts to a range of 33 to 44 kJ mol^{-1} ; this also implies that back dissociation of $\mathbf{1}$ into the reactants is favored over crossing TS1/3. Whereas the triplet analogue of intermediate $\mathbf{3}$ has a lower energy (triplets are indicated by a superscript t), in the region of TS1/3 the triplet surface is located ca. 50 kJ mol^{-1} above the singlet PES. Hence, we expect the minimum-energy crossing point from the singlet to the triplet surface to be located between TS1/3 and $\mathbf{3}$, but we did not calculate it explicitly.^[16]

Starting from the triplet biradical $\mathbf{3}$ a low-energy intermediate $\mathbf{4}$ (Figure 3) is reached in a complex, but energetically facile rearrangement. Again, complete details will be given elsewhere.^[15] Here, it may suffice to note that the highest point between $\mathbf{3}$ and $\mathbf{4}$ is 90 kJ mol^{-1} below the entrance channel of separated $[\text{V}_3\text{O}_7]^+ + \text{C}_3\text{H}_8$.

In conclusion and in agreement with the experimental observations, neither of the two pathways of initial C–H activation allow the system to cross the barrier. The DFT calculations further suggest that the observed formal $[\text{V}_3\text{O}_7(\text{C}_3\text{H}_8)]^+$ adduct does indeed correspond to the association complex $\mathbf{1}$ and does not contain new subunits, such as a propene ligand together with two OH groups.

For the reactions of 1-butene with $[\text{V}_3\text{O}_7]^+$ (Figure 1b), DFT calculations for the closed-shell singlet state predict the reaction to be more exothermic than for propane (-174 ^[15] vs. -158 kJ mol^{-1}) and also predict formation of a substantially much stronger association complex with $[\text{V}_3\text{O}_7]^+$ ($\mathbf{6}$, Scheme 1, Figure 4). The intrinsic barrier for the [2+2] addition to the V=O bond is also lower for the allylic C–H bond in 1-butene (TS6/7, Scheme 1) than for the secondary C–H bond of propane (91 vs.

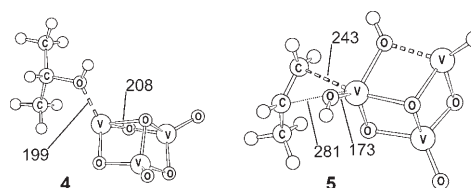


Figure 3. Structures of intermediates $\mathbf{4}$ and $\mathbf{5}$.

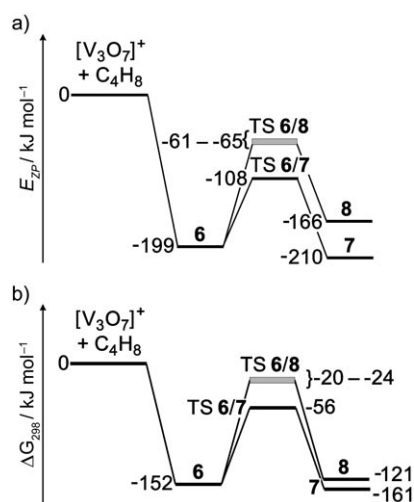


Figure 4. Initial C–H activation steps in the reaction of 1-butene with $[V_3O_7]^+$. a) Relative energies (E_{ZP} at 0 K) and b) free energies (ΔG_{298}).

120 kJ mol^{-1}). As a result, TS6/7 is so much below the entrance channel of $[V_3O_7]^+ + 1\text{-butene}$ (Figure 4) that this energy difference is not compensated for by the entropy gain for the back decomposition into reactants as seen from a strongly negative $\Delta G_{298} = -56 \text{ kJ mol}^{-1}$. This computational result is in perfect agreement with the experimentally observed efficient ODH of 1-butene by $[V_3O_7]^+$ (Table 1). For completeness we note that the open-shell transition structure for hydrogen abstraction, TS6/8, is higher in energy than TS6/7, but is also still significantly below the entrance channel (Figure 4).

In order to further test the DFT-based predictions experimentally, the potential energy surface of the $[V_3O_7]^+/\text{propane}$ system has also been approached from the product side. Thus, exclusive formation of $[V_3O_7H_2]^+$ concomitant with neutral propene is observed in the reactions of $[V_3O_6]^+$ with 1- and 2-propanol (Table 1). The slightly enhanced reactivity of 1-propanol is consistent with linear alcohols being less sterically hindered than branched alcohols. The complementary process, that is, addition of the propene ligand to $[V_3O_6]^+$ concomitant with loss of neutral water, is not observed with either of the isomeric alcohols. This result can be attributed to the fact that an electron-deficient species such as a high-valent metal oxide cation prefers coordination with water as a better σ -donor ligand rather than with a typical π ligand such as an alkene.^[17] Furthermore, the reaction of mass-selected $[V_3O_7H_2]^+$ with propene leads to mere molecular addition of the olefin. These results fully support the computational predictions, in that the reaction of $[V_3O_6]^+$ and propanol can smoothly proceed from the entrance channel to the products $[V_3O_7H_2]^+$ and propene, while deoxygenation of the alcohol to yield $[V_3O_7]^+ + C_3H_8$ via the entropically disfavored TS1/2 ($\Delta G_{298} = 59 \text{ kJ mol}^{-1}$) is unable to compete (Figure 2).

In summary, although the ODH reaction of propane by $[V_3O_7]^+$ is exothermic, this vanadium oxide cation is not capable of dehydrogenating propane because of the presence of a significant barrier associated with the initial C–H activation. In marked contrast, 1-butene reacts with $[V_3O_7]^+$

at thermal energies. These experimental results perfectly agree with the DFT calculations, which predict C–H activation as the rate-determining step. The differences between propane and 1-butene can mostly be traced back to the energy gained upon initial coordination of the hydrocarbon by the vanadium oxide cation and the more facile activation of an allylic C–H bond.

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.^[20] Briefly, $[V_mO_n]^+$ clusters of interest were generated by ESI of $V_6O_7(OCH_3)_{12}$ dissolved in CD_3OD ,^[21,22] mass-selected using Q1, allowed to interact with propane or 1-butene, at pressures on the order of 10^{-4} mbar, which approximately corresponds to single-collision conditions, and the ionic products were then mass-analyzed using Q2. Ion-reactivity studies were performed at an interaction energy in the hexapole (E_{lab}) nominally set to 0 eV. The reaction products formed rapidly decline at elevated collision energies, thereby justifying the assumption that these processes occur at quasi-thermal energies.^[14]

The calculations were performed using the hybrid density functional B3LYP^[23] with triple- ζ plus polarization basis sets (TZVP)^[24] employing Turbomole 5.7.^[25] B3LYP was shown previously to describe $[V_mO_n]$ clusters in good agreement with available experimental data as well as quantum chemical methods that explicitly include electron correlation.^[3c] The unrestricted Kohn–Sham scheme was used to deal with triplet spin states. For open-shell singlets, broken-symmetry calculations were performed,^[26] and the low-spin energy was obtained from the triplet and broken-symmetry energies by spin projection.^[27] When the expectation value of S^2 significantly deviated from one (indicating an increasing overlap between the unpaired electrons), as was the case for TS1/3, spin-projection was questioned^[28] and both energies were then taken as limiting estimates, as indicated by the grey-shaded boxes in Figures 2 and 4. All intermediates and transition structures were characterized by frequency analysis, and the energies include corrections for zero-point vibrations. Energies, entropies, and Gibbs free energies at room temperature can be found in the Supporting Information.

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