Vanadium oxides are employed as efficient oxidation cata-
ysts in various processes such as the oxidative dehydrogen-
ation 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\text{]}^+)\], corroborated by
quantum chemical calculations using density functional
theory (DFT). The cation [\(\text{V}_3\text{O}_7\text{]}^+)\] was chosen because it
represents the smallest polynuclear V/O cluster cation con-
taining only formal V\(^{V\text{\text{I}}\text{\text{I}}})\]. 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\text{]}^+)\]. In general, oxidative

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under http://www.angewandte.org or from the author.
dehydrogenation (ODH) of hydrocarbons involves reduction of the metal center ([V3O8]2- + 2H+ + 2e- → [V3O7]3-). 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 resulting in the dehydrogenation of butane to butadiene (C4H8 + 2H → C4H6). 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 [V3O7]2- to form [V3O7(C3H8)]2-, or neutral water may be eliminated while the dehydrogenated hydrocarbon remains bound at the metal oxide cation to yield [V3O6(C3H6)]3- and [V3O7- (C2H4)]2-, respectively.

The experimental investigation of the [V3O7]2- /hydrocarbon systems uses a quadrupole-based mass spectrometer equipped with an electrospray-ionization source.[14] Ion–molecule reactions (IMRs) of mass-selected [V3O7]2- with propane formally result in molecular addition of the hydrocarbon to the vanadium oxide ion to form [V3O7(C3H8)]2- (Figure 1a) and yields no products indicative for an ODH process. In contrast, oxidative dehydrogenation to yield [V3O7H2]2- concomitant with formation of neutral butadiene is indeed observed in the reaction of mass-selected [V3O7]2- with 1-butene (Figure 1b, Table 1). In addition, four minor product channels are associated with C–C bond cleavage to lead to the corresponding [V3O7(C3H6)]2- cation with parallel elimination of ethene, mere association to form [V3O7- (C2H4)]2-, 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 [V3O7]2- originate specifically from the C3 and C4 positions of 1-butene. We note in passing that the product ion [V3O7H2]2- displays a dihydroxide structure rather than that of a water complex, that is, [V3O7(OH)2]2- rather than [V3O7(OH3)]2-.

To understand why ODH is not observed when [V3O7]2- 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 [V3O7]2- starts with formation of the remarkably stable (–107 kJ mol–1) ion–molecule complex (Scheme 1, Figure 2). The secondary carbon atom of propane attaches to a vanadium site, and the [V3O7]2- 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 V=O unit yielding intermediate 2 (–166 kJ mol–1). These steps involve only closed-shell singlet species. The transition structure TS 1/2 lies 13 kJ mol–1 above the separated reactants. In the reaction of ethane and propane with the formal V3 compound [VO3]2-, addition of C–H bonds across a V≡O unit has also been identified as an initial step, although in these systems the transition structures are below the respective entrance channels because [VO3]2- binds alkanes more strongly.[12a,13a] In a thermal gas-phase reaction, TS 1/2 constitutes a bottleneck because dissociation of the

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

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>krel</th>
</tr>
</thead>
<tbody>
<tr>
<td>[V3O7]2- + C3H8 + C2H4</td>
<td>[V3O7(C3H8)]2- (100)</td>
<td>0.03</td>
</tr>
<tr>
<td>[V3O7]2- + C2H5OH</td>
<td>[V3O7(C2H5OH)]2- (25)</td>
<td>1.00</td>
</tr>
<tr>
<td>[V3O7]2- + CH3COCH3</td>
<td>[V3O7(C2H5)]2- (82)</td>
<td>0.63</td>
</tr>
<tr>
<td>[V3O7]2- + C2H5OH</td>
<td>[V3O7(C2H4)]2- (100)</td>
<td>0.24</td>
</tr>
<tr>
<td>[V3O7]2- + C3H8</td>
<td>[V3O7H2(C3H8)]2- (64)</td>
<td>0.24</td>
</tr>
<tr>
<td>[V3O7]2- + CH3CN</td>
<td>[V3O7H2(C3H6)]2- (64)</td>
<td>0.24</td>
</tr>
</tbody>
</table>

[a] Branching ratios in brackets. [b] Relative rates normalized to this reaction. [c] The reaction of bare Pt with CH4 was used as a reference to convert the relative rate constant (krel) into absolute values, which leads for the reaction of [V3O7]2- with C2H5OH to krel = (1.3 ± 0.2) × 103 cm3 mol–1 s–1.[14] The collision rate constant amounts to 1.4 × 104 cm3 mol–1 s–1.[9] [d] The primary ionic products rapidly add butene to yield [V3O7H2(C3H8)]2-; see Figure 1b.

**Figure 1:** IMRs of [V3O7]2- with a) propane and b) 1-butene. p(hydrocarbon) = 2.5 × 10–2 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 1-butene by [V3O7]−. Selected distances are given in pm, and triplets are indicated by a superscript t.  < S > : spin operator value (see the Experimental Section and the Supporting Information).

Figure 2. a) Relative energies (E0 at 0 K) for the reaction pathways for oxidative dehydrogenation of propane by [V3O7]−. The transition from 3 to 4 involves a complex rearrangement over several steps which will be described elsewhere. 15 b) Free energies (ΔG0) for the initial C–H activation steps. Triplets are indicated by a superscript t.

Figure 3. Structures of intermediates 4 and 5.
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In order to further test the DFT-based predictions experimentally, the potential energy surface of the $[V_3O_7]^-$ was mapped out for the reaction of mass-selected $[V_3O_7H_2]^-$ with neutral propene is observed in the reactions of $[V_3O_6]^-$ with water as a better reactant. Thus, exclusive formation of $[V_3O_7H_2]^-$ and propane and 1-butenene can mostly be traced back to the energy difference of the entrance channel of $[V_3O_7]^-$ that 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.[15] Briefly, $[V_3O_7]^-$ clusters of interest were generated by ESI of $V_2O_5(OCH_3)_2$ dissolved in CD$_3$OD to 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 ($E_{int}$) 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.[16]

The calculations were performed using the hybrid density functional B3LYP[20] with triple-$\zeta$ plus polarization basis sets (TZV)[20] employing Turbomole 5.7.[23] B3LYP was shown previously to describe $[V_3O_7]$ clusters in good agreement with available experimental data as well as quantum chemical methods that explicitly include electron correlation.[14] The unrestricted Kohn–Sham scheme was used to deal with triplet spin states. For open-shell singlets, broken-symmetry calculations were performed,[24] and the low-spin energy was obtained from the triplet and broken-symmetry energies by spin projection.[25] 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[25] 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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