Gas-phase reactions of V$_2$O$_5^+$ and V$_2$O$_6^+$ ions with CH$_3$CF$_3$
studied by density functional theory

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Abstract

The present work presents a computational study (B-P86 density functional, D(T)ZVP basis set) of structure and energetics of V$_2$O$_n^+$ cations ($n$=5–6) and their gas-phase reactivity toward CH$_3$CF$_3$. Both V$_2$O$_5^+$ and V$_2$O$_6^+$ are shown to have an asymmetric double-bridge structure, (O)$_2$–V–(O)$_2$–V(O) and (O$_2$)(O)–V–(O)$_2$–V(O) in their respective stablest configurations. The V$_2$O$_5^+$ cation has a terminal peroxy ligand. The cations can form weakly bound V$_2$O$_n^+$·CH$_3$CF$_3$ adducts with CH$_3$CF$_3$. The latter can rearrange to much stabler CH$_3$CF$_2$O(O$_n^K_4$)V(O$_2$)V(O)F alkoxy structures. The formation of V$_2$O$_n^+$·CH$_3$CF$_3$ from V$_2$O$_n^+$ and free CH$_3$CF$_3$ is very exothermic. The C–C bond cleavage in V$_2$O$_6^+$·CH$_3$CF$_3$ to yield V$_2$O$_5^+$·CF$_3$ and the free CH$_3$ radical is much more energy demanding that the analogous dissociation of V$_2$O$_5^+$·CH$_3$CF$_3$, which accounts for dissimilarity in experimental behavior of V$_2$O$_5^+$ and V$_2$O$_6^+$ and agrees with the observation that V$_2$O$_5^+$ but not V$_2$O$_6^+$ renders the CH$_3$–CF$_3$ cracking. Another route of the cracking, with release of CF$_3$, is not possible because the stablest configurations of V$_2$O$_n^+$·CH$_3$CF$_3$, contain an intact methyl group but no CF$_3$.

The abstraction of HF from CH$_3$CF$_3$ is computed to be roughly equally favorable, with $\Delta E$ of about $-80$ kJ mol$^{-1}$ for both V$_2$O$_5^+$·HF and V$_2$O$_6^+$·HF.

The direct dissociation of O$_2$ from V$_2$O$_6^+$ requires $142$ kJ mol$^{-1}$ only, while the alternative mechanisms are more exothermic. This confirms the experimentalists’ assumption that dioxygen dissociation from V$_2$O$_6^+$ is a collision-induced dissociation.

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Keywords: Vanadium oxide cations; DFT calculations; Gas-phase reactivity; C–C bond cracking

1. Introduction

Interest in gas phase clusters of metal oxides arises from the question how the properties and the reactivity of metal oxides scale with their aggregation level from small molecules over nano-sized clusters up to the bulk solid. Vanadium oxide clusters are of special interest since solid materials catalyze a broad range of reactions, from SO$_2$→SO$_3$ oxidation to oxidative dehydrogenation of alkanes [1–3]. Their catalytic activity is known to depend on the distribution of active metal oxide species on supports such as silica or alumina.

Studies on vanadium oxides include cluster cations [4–9] and cluster anions [10–13]. Gas phase studies focus on charged clusters, cations or anions, because they are much easier to identify and to separate by mass spectrometric techniques than neutral species. Cationic metal oxide clusters are generated directly by laser vaporization of vanadium metal in the presence of oxygen under plasma conditions and subsequently separated by mass spectrometry. The stabllest cations correspond to the (VO$_5^+$)$_n$(V$_2$O$_5^+$)$_m$(O$_2$)$_q$ composition. In oxygen-rich clusters (formal oxidation number about or greater than 5), O$_2$ units were shown to be only weakly bound to the (VO$_5^+$)$_n$(V$_2$O$_5^+$)$_m$ moiety. Bell et al. studied the reactivity of cationic vanadium oxide cluster towards the halogenated hydrocarbons CH$_3$F$_2$ [7], CCl$_4$ [8], and C$_2$F$_6$ and CH$_3$CF$_3$ [5]. With respect to CH$_3$CF$_3$, vanadium oxide clusters V$_2$O$_5^+$·7, V$_2$O$_5^+$·9, V$_4$O$_{16}$·11, V$_4$O$_{11}$·13, V$_5$O$_{13}$·16, and V$_7$O$_{16}$·18 show versatile reactivity including HF elimination, cracking of the carbon–carbon bond, and replacement of two fluorine atoms by one oxygen. In particular, two smaller-size clusters V$_2$O$_5^+$ and V$_2$O$_5^+$ yield a plenty of products: V$_2$O$_5^+$ gives V$_2$O$_5^+$·F$_2$, V$_2$O$_5^+$·HF, and V$_2$O$_5^+$·CF$_3$. Note that the V$_2$O$_5^+$·CF$_3$ formation actually

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means the CH$_3$–CF$_3$ bond cleavage (cracking). V$_2$O$_5^+$ displays V$_2$O$_6^-$·HF as well as V$_2$O$_5^+$·F$_2$ and V$_2$O$_4^+$, the latter two being dioxygen dissociation products, but no cracking products were found for V$_2$O$_6^+$. Some of the larger V$_n$O$_m^+$ clusters also afford V$_n$O$_{n-1}^+$·F$_2$ and V$_n$O$_{n-2}^+$·HF products. In addition, the oxygen-rich clusters display dioxygen loss yielding V$_n$O$_{n-1}^+$·F$_2$ and V$_n$O$_{n-2}^+$·F$_2$, but the C–C bond cracking did not take place. The simple dioxygen release V$_n$O$_m^+$→V$_n$O$_{m-2}^+$ was attributed to the collision-induced dissociation, since this is the only chemical process that occurs if C$_3$F$_6$ is used as the reactant gas.

While mass spectrometry is able to identify charged reactants and products and provides information about their composition, determination of geometric structures of clusters remains a challenge for experimentalists. Some information can obtained from photoelectron spectra [12,13] or, as recently shown, from IR spectra when advanced techniques of laser spectroscopy are used [14,15].

To contribute to the understanding of reactions of vanadium oxide cluster cations with CH$_3$CF$_3$, we report structures and energies of reactants, products and possible intermediates. Because of the large variety and complexity of the V$_n$O$_m^+$ cations found in vanadium metal vapor under plasma conditions in the presence of oxygen [5], as a first step we focus on the examination of two specific cations, V$_2$O$_5^+$ and V$_2$O$_6^+$, which exhibit most versatile reactivity. The structures of V$_2$O$_5^+$ and V$_2$O$_6^+$ have been reported before by Calatayud et al. [16,17]. Gracia et al. recently reported DFT mechanistic studies of reactions of the small VO$_2^+$ ion with ethane [18] and ethene [19].

2. Computational methods

The present study employs Becke’s exchange functional [20] in combination with Perdew’s correlation functional [21] (BP86). For open-shell systems, spin-unrestricted, otherwise restricted Kohn–Sham equations are solved. The BP86 functional as other gradient-corrected functionals permits substantial savings of computation time compared to hybrid functionals (B3LYP) when the RI-DFT (‘resolution of identity’) procedure [22] is applied. Comparison for neutral closed-shell (V$_2$O$_5$)$_n$ clusters shows that B3LYP and BP86 yield very similar structures and energies [23], while for electron affinities the BP86 functional gave even superior results [24].

The calculations were performed with all-electron double-$\zeta$ valence basis sets on vanadium (DZVP, contraction scheme {842111/63111/4111}), triple-$\zeta$ valence basis set on oxygen, carbon, and fluorine (TZVP, {62111/4111/111}), and triple-$\zeta$ basis set on hydrogen (TZP, {3111/1111}) as described by Ahlrichs and co-workers [25,26] augmented by a set of polarization functions (a $p$-set for vanadium, a $d$-set for oxygen, carbon, and fluorine). We refer to this mixed basis set as D(T)ZVP. Extensive tests reported previously [23,24] showed that the results obtained are virtually identical to the full TZVP ones.

All geometry optimizations were performed with the TURBOMOLE program package [27]. To characterize the stationary points found by optimization, harmonic force constants were calculated analytically for the stabllest structures found for each class.

3. Results

3.1. Structures and electronic states of different isomers of V$_2$O$_n^+$ cations (n = 4–6).

3.1.1. V$_2$O$_5^+$

As reported recently [28], this cation consists of a four-membered V–(O)–V ring with two terminal O atoms in trans position (Fig. 1). It has C$_{2v}$ symmetry. An alternate less symmetric C$_4$ structure [28] is not found at BP86 level, although it is stabler at B3LYP level. The cis structure (C$_2v$, symmetry, $^2A_1$ state) is 20.2 kJ mol$^{-1}$ higher in energy, which is in very well agreement with B3LYP results by Asmis et al. [15]. Note that higher-correlated ab initio calculations of Pykavy et al. [28] gave 8.4 kJ mol$^{-1}$ for cis/trans energy gap. The V atoms in V$_2$O$_5^+$ have a formal (d$^1$, d$^0$) occupation, the unpaired electron occupies a MO that is a linear combination of d orbitals of both vanadium atoms. This gives rise to a variety of doublet states. The BP86 calculations indicate that the $^2A_g$ state is the ground state of V$_2$O$_5^+$. In the case of the cis structure, the $^2A_1$ state is the ground state of V$_2$O$_5^+$, with the $^2B_2$ and $^2A_2$ states being 25.4 and 43.6 kJ mol$^{-1}$ above, respectively.

3.1.2. V$_2$O$_6^+$

For the neutral V$_2$O$_5$ molecule (d$^0$ configuration of V), previous studies found the doubly-bridged structure V(O)$_2$–V(O)$_2$–VO stabler than the singly-bridged V(O)$_2$–O–V(O)$_2$...
one [23,16]. In accord with Calatayud et al. [16] our BP86 calculations predict that for the V$_2$O$_5^+$ cation the doubly-bridged structure (Fig. 1) is by 65 kJ mol$^{-1}$ more stable than the singly-bridged one (Fig. 1). In the $^2A'$ ground state the unpaired electron occupies an $a'$ orbital which corresponds to the HOMO of V$_2$O$_5$. The first excited state of V$_2$O$_5^+$, $^2A''$, lies 65.3 kJ mol$^{-1}$ above the ground state. Structurally, the cation differs from the neutral V$_2$O$_5$ mainly in that the two V1=O bonds are elongated by 2 and 5 pm. Upon ionization of V$_2$O$_5$ the electron is removed from a bonding V1=O orbital.

For the singly bridged structure of V$_2$O$_5^+$ two doublet states, $^2B$ and $^2A$, are nearly degenerate at BP86 level. The B3LYP functional yields a $C_1$ structure as the most favorable.

3.1.3. V$_2$O$_6^+$

A V$_2$O$_6^+$ cluster can be generated from V$_2$O$_5^+$ either by adding an O ligand to a vacant binding site on V or by replacing an O atom of V$_2$O$_5^+$ by a peroxo ligand. The latter gives rise to a variety of isomers with a peroxo group shown in Fig. 2. The energetically lowest is the (O$_2$)(O)V=O=V(O) structure with a trans configuration of the vanadyl groups ($C_1$ symmetry). The energy difference between the cis and trans isomers is minor. The isomer with a peroxo group at one V and two terminal O atoms on the other V atom is much less stable (192.4 kJ mol$^{-1}$ above the lowest configuration). Adding an oxygen to V of V$_2$O$_5^+$ yields a symmetric O$_2$V=O=VO$_2$ isomer with two terminal O atoms on both V atoms ($D_{2h}$) is obtained. This structure is not particularly stable, its $^4B_{3u}$ ground state is 225 kJ mol$^{-1}$ above the stablast peroxo structure. Another possibility is adding an O atom to a vanadyl oxygen of V$_2$O$_5^+$ forming a superoxo V$_2$O$_6^+$ structure. Alternatively, this structure can also be created by forming a complex between V$_2$O$_5^+$ ($^2A_1$) and O$_2$ ($^3\Sigma$). The spins can be coupled either into a doublet or a quartet. The doublet superoxo structure is 68.6 kJ mol$^{-1}$ above the peroxo structure and the quartet structure 106.1 kJ mol$^{-1}$. The latter has a longer V–O2 distance of 219 pm compared to 183 pm for the doublet. It should be rather considered a complex of the V$_2$O$_5^+$ cation with a dioxygen molecule in its triplet ground state.

Starting from the singly bridged V$_2$O$_5^+$ structure, singly bridged peroxo and superoxo structures can also be generated, but these are less stable than their doubly bridged counterparts. The stablast singly bridged structure is the peroxo structure (O$_2$)(O)V=O=V(O) which is 83.3 kJ mol$^{-1}$ above the global minimum structure. This is the only singly bridged isomers which is stable with respect to dissociation into V$_2$O$_5^+$ and O$_2$. Replacement of a bridging oxygen atom in V$_2$O$_5^+$ by the $\mu$-O$_2$ ligand would lead to a (O$_2$)V=O(O2)–V(O).

The doubly bridged peroxo structure (O$_2$)(O)V=O=VO$_2$ in the singlet state is also the stablast isomer of the neutral V$_2$O$_6$. It is 306 kJ mol$^{-1}$ more stable than the O(O)V=O=V(O) structure reported in paper [24]. In the neutral peroxo structure, the V–O$\text{peroxo}$ bonds are about 13 pm shorter than in the cation, and, correspondingly, the O–O bond is longer by 11 pm. This is a consequence of the fact that the HOMO of V$_2$O$_6$, from which the electron is removed, is essentially the anti-bonding O–O orbital. The triplet state is 12.9 kJ mol$^{-1}$ less favorable. The second stablast V$_2$O$_6$ species O$_2$V=O=VO$_2$ (triplet state) is 10.4 kJ mol$^{-1}$ less stable than the singlet O$_2$V=O=VO$_2$.

![Fig. 2. Calculated structures of the V$_2$O$_5^+$ ion. Notations are the same as in Fig. 1.](image)
3.1. Ionization potentials

The calculated vertical ionization potentials (IP) of the $\text{V}_2\text{O}_5 (\text{C}_s, 1\text{A}_0/2\text{A}_0)$ and $\text{V}_2\text{O}_6 (\text{C}_1, 1\text{A}/2\text{A})$ clusters are 10.5 and 9.5 eV, respectively. The IP depends on the nature of the orbital the electron is removed from. The HOMO of both $\text{V}_2\text{O}_5$ and $\text{V}_2\text{O}_6$ is an oxygen $p$-orbital, but it is non-bonding in the case of $\text{V}_2\text{O}_5$ and anti-bonding for $\text{V}_2\text{O}_6$. Consequently, the IP of $\text{V}_2\text{O}_5$ is about 1 eV higher than that of $\text{V}_2\text{O}_6$.

3.2. Dioxygen and oxygen loss

A very important reaction typical of nearly all oxygen-rich $\text{V}_n\text{O}_m^+$ cations is loss of molecular oxygen to form $\text{V}_n\text{O}_m^-$. It was observed for $\text{V}_2\text{O}_6^+$ and $\text{V}_3\text{O}_7^+$, but not for $\text{V}_2\text{O}_5^+$ or $\text{V}_3\text{O}_6^+$. An obvious explanation is the presence of a peroxo ligand. The dissociation of the peroxo $\text{V}_2\text{O}_6^+$ (Fig. 2) into trans $\text{V}_2\text{O}_4^+$ (3$^1\Sigma^+$) and $\text{O}_2$ (3$^3\Sigma^-$) is endothermic with $\Delta E = +142.2$ kJ mol$^{-1}$. For the superoxo complex ‘III’ in the doublet state, $\Delta E = +73.5$ kJ mol$^{-1}$, which agrees with the value reported by Calatayud et al. [16] (+74 kJ mol$^{-1}$). Note that the higher-energy $\text{V}_2\text{O}_6^+$ species ‘V–VII’ are not bound with respect to dissociation into $\text{V}_2\text{O}_4^+$ and $\text{O}_2$ ($\Delta E > 0$).

Loss of atomic oxygen (3$^3P$) from $\text{V}_2\text{O}_6^+$ and $\text{V}_2\text{O}_5^+$ requires 331 and 386 kJ mol$^{-1}$. Calatayud et al. [16] report 332 and 264 kJ mol$^{-1}$. Evidently, the latter value is underestimated because not the stablest isomer of $\text{V}_2\text{O}_5^+$ was used for its evaluation in Ref. [16].

3.3. Reaction of $\text{V}_2\text{O}_5^+$ with CH$_3$CF$_3$

3.3.1. $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ adduct

Formation of the $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ adduct is likely to be the starting point for the reaction of $\text{V}_2\text{O}_5^+$ with CH$_3$CF$_3$. CH$_3$CF$_3$ will preferably attack the V atom with a free coordination site, i.e. the V6 atom with only one vanadyl group. In the attempt to optimize the $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ structure with the CF$_3$ group directed toward the electro-positive vanadium atom V6, one fluorine atom is transferred to form a normal covalent bond to V6 such that the adduct becomes essentially $\text{V}_2\text{O}_5\text{F} \cdots \text{CF}_2\text{CH}_3$ (II on Fig. 3). Since this structure is the direct optimization result, we conclude that the reaction

$$\text{V}_2\text{O}_5^+ + \text{CH}_3\text{CF}_3 \rightarrow \text{V}_2\text{O}_5\text{F} \cdots \text{CF}_2\text{CH}_3$$

proceeds with no or only a very small barrier. The reaction energy is $-156$ kJ mol$^{-1}$.

Attack of CH$_3$CF$_3$ from the CH$_3$ side involves a hydrogen transfer from the CH$_3$ group to one of the oxygen atoms. Subsequently, the CH$_2$CF$_3$ moiety rotates to enable the formation of a O–H···F hydrogen bond (structure ‘III’, Fig. 3). This complex is less stable than $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ (II), but its formation is still favorable with $\Delta E = -104$ kJ mol$^{-1}$.

There is, however, another set of the $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ structures which are substantially stabler that those described above. The energetically lowest structure found is ‘XIII’, (Fig. 3) which is as much as 181 kJ mol$^{-1}$ more
3.3.3. Formation of the cracking product $V_2O^+_5\cdot CH_2CF_3$

The cracking product $V_2O^+_5\cdot CH_2CF_3$ is expected to be formed from a $V_2O^+_5\cdot CH_2CF_3$ adduct by splitting off the CH$_3$ group. The process conceivable for formation of the stables $VIII$ from $V_2O^+_5\cdot CH_2CF_3$ species is methyl abstraction from $XIII$. It takes 215.5 kJ mol$^{-1}$, which is only about a half of the unsupported CH$_2CF_3 \rightarrow CH_3 + CF_3$ dissociation energy ($\Delta E = +419$ kJ mol$^{-1}$). The experimental value for the latter is 423.4 $\pm$ 4.6 kJ mol$^{-1}$ [29].

On the other hand, the methyl dissociation from $V_2O^+_5\cdot CH_2CF_3$ ‘VII’ isomer to give $V_2O^+_5\cdot CF_3$ ‘VII’ has a dissociation energy of $+42$ kJ mol$^{-1}$ only.

The entire cracking reaction

$V_2O^+_5 + CH_2CF_3 \rightarrow CH_3 + V_2O^+_5\cdot CF_3$ (“XIII”) proceeds through three exothermic steps

$V_2O^+_5 + CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_2CF_3$ “II”

($\Delta E = -156.0$ kJ mol$^{-1}$),

$V_2O^+_5\cdot CH_2CF_3$ “II” $\rightarrow V_2O^+_5\cdot CH_2CF_3$ “VI”

($\Delta E = -45.3$ kJ mol$^{-1}$), and

$V_2O^+_5\cdot CH_2CF_3$ “VI” $\rightarrow V_2O^+_5\cdot CH_2CF_3$ “XIII”

($\Delta E = -181.1$ kJ mol$^{-1}$),

and one endothermic step,

$V_2O^+_5\cdot CH_2CF_3$ “XIII” $\rightarrow V_2O^+_5\cdot CF_3 + CH_3$

($\Delta E = +215.5$ kJ mol$^{-1}$).

The total reaction energy is $-167$ kJ mol$^{-1}$ (Table 1).

### 3.3.4. Formation of $V_2O^+_5\cdot HF$

HF abstraction from CH$_3$CF$_3$ was observed for both $V_2O^+_5$ and $V_2O^+_5$ clusters. For the $V_2O^+_5\cdot HF$ cluster, a few structures are possible depending on the proton position, which can be attached either to a terminal or bridging oxygen (Fig. 5).

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$n = 5$</th>
<th>$n = 6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>$V_2O^+_5 + CH_2CF_3 \rightarrow (V_2O^+_5\cdot CH_2CF_3)^+$</td>
<td>$-382.3$</td>
</tr>
<tr>
<td>1b</td>
<td>$(V_2O^+_5\cdot CH_2CF_3)^+ \rightarrow V_2O^+_5\cdot CH_3 + CH_3$</td>
<td>$+215.5$</td>
</tr>
<tr>
<td>1c</td>
<td>$(V_2O^+_5\cdot CH_2CF_3)^+ \rightarrow V_2O^+_5\cdot CH_3 + CF_3$</td>
<td>$+340.8$</td>
</tr>
<tr>
<td>2a</td>
<td>$V_2O^+_5\cdot CH_2CF_3 + CH_3 \rightarrow V_2O^+_5\cdot CH_3 + CH_2CF_3$</td>
<td>$-166.8$</td>
</tr>
<tr>
<td>2b</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CF_3 + CH_2CF_3$</td>
<td>$586.2$</td>
</tr>
<tr>
<td>2c</td>
<td>$V_2O^+_5\cdot CH_2CF_3 + CH_3 \rightarrow V_2O^+_5\cdot CH_3 + CH_2CF_3$</td>
<td>$+460.9$</td>
</tr>
<tr>
<td>3</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_3 + CH_3$</td>
<td>$-41.6$</td>
</tr>
<tr>
<td>4</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_3 + CF_3$</td>
<td>$-78.5$</td>
</tr>
<tr>
<td>4a</td>
<td>$(V_2O^+_5\cdot CH_2CF_3)^+ \rightarrow V_2O^+_5\cdot CH_3 + CH_3$</td>
<td>$+303.8$</td>
</tr>
<tr>
<td>5</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_3 + CF_3$</td>
<td>$-176.1$</td>
</tr>
<tr>
<td>5a</td>
<td>$(V_2O^+_5\cdot CH_2CF_3)^+ \rightarrow V_2O^+_5\cdot CH_3 + CH_3$</td>
<td>$+206.3$</td>
</tr>
<tr>
<td>6</td>
<td>$(V_2O^+_5\cdot CH_2CF_3)^+ \rightarrow V_2O^+_5\cdot CH_3 + CF_3$</td>
<td>$+313.6$</td>
</tr>
<tr>
<td>7</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_3 + O_2$</td>
<td>$-142.2$</td>
</tr>
<tr>
<td>8</td>
<td>$V_2O^+_5\cdot CH_2CF_3 \rightarrow V_2O^+_5\cdot CH_3 + OO$</td>
<td>$-414.6$</td>
</tr>
</tbody>
</table>
The stablest configuration of $\text{V}_2\text{O}_5^+$ is ‘I’ which contains the fluoro and hydroxo ligands in geminal position to each other. The $\Delta E$ energy for the overall reaction

$$\text{V}_2\text{O}_5^+ + \text{CH}_3\text{CF}_3 \rightarrow \text{V}_2\text{O}_5^+ \cdot \text{HF} + \text{CH}_2\text{CF}_2$$

is $-78.5$ kJ mol$^{-1}$.

A straightforward way for this reaction includes the shift of the CF$_3$CH$_2$ group in $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ ‘IX’ with a subsequent or simultaneous transfer of the F atom from CF$_3$CH$_2$ to the V atom. This process is endothermic ($\Delta E = +206$ kJ mol$^{-1}$). Another possibility is the CH$_2$CF$_2$ elimination from $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ ‘VII’ or ‘VIII’, which leads to $\text{V}_2\text{O}_5^+ \cdot \text{HF}$ ‘I’ ($+123.6$ and $+127.7$ kJ mol$^{-1}$, respectively).

### 3.4. Reaction of $\text{V}_2\text{O}_6^+$ with CH$_3$CF$_3$

#### 3.4.1. $\text{V}_2\text{O}_6^+ \cdot \text{CH}_3\text{CF}_3$ adduct

Similarly to $\text{V}_2\text{O}_5^+ \cdot \text{CH}_3\text{CF}_3$ case, the primary product formed from $\text{V}_2\text{O}_6^+$ and CH$_3$CF$_3$ is a fluoride transfer product $\text{V}_2\text{O}_6\text{F} \cdots \text{CF}_2\text{CH}_3$ (‘II’ in Fig. 6). This process is exothermic ($\Delta E = -145$ kJ mol$^{-1}$). CH$_2$CF$_2$ alkyl shift in ‘II’ leads to ‘III’ or ‘VII’, which are 27 and 67 kJ mol$^{-1}$ more favorable than ‘II’. For the CH$_3$-side attack, hydrogen transfer from the CH$_3$ group to an oxygen atom is also possible, but differently from the $\text{V}_2\text{O}_5^+$ case the respective $\text{V}_2\text{O}_6^+ \cdot \text{CH}_3\text{CF}_3$ product ‘IV’ is thermodynamically unstable ($\Delta E = +83$ kJ mol$^{-1}$).

There are a number of $\text{V}_2\text{O}_6^+ \cdot \text{CH}_3\text{CF}_3$ structures that have a C–C bond cleaved. ‘XI’ and ‘XIV’ could be formed by methyl shift from ‘VII’; these reactions are slightly endothermic ($\Delta E = +7$ and $+4$ kJ mol$^{-1}$, respectively). By far stabler than the others $\text{V}_2\text{O}_6^+ \cdot \text{CH}_3\text{CF}_3$ structures is ‘XV’, which is 126.1 kJ mol$^{-1}$ below ‘VII’. This structure is remarkably different from the others in that there are neither terminal nor bridging peroxy groups. It has two tetrahedrally coordinated vanadium(V) atoms connected by a single oxygen bridge. This cation is coordinatively saturated complex, which certainly contributes to its high stability. Note that among the $\text{V}_2\text{O}_6^+ \cdot \text{CH}_3\text{CF}_3$ family, a similar role of saturated structures is played by doubly bridged ‘XIII’ and ‘XIV’ (Fig. 3), the formation of which is similarly exothermic.

#### 3.4.2. Characterization of $\text{V}_2\text{O}_6^+ \cdot \text{CF}_3$

Among the $\text{V}_2\text{O}_6^+ \cdot \text{CF}_3$ isomers formally obtained by adding a CF$_3$ group to $\text{V}_2\text{O}_6^+$, ‘III’ with a terminal CF$_3$ ligand is the stablest, whereas ‘IV’ containing a V–C bond is very high in energy (Fig. 7). As is for $\text{V}_2\text{O}_5^+ \cdot \text{CF}_3$, the structures with separated OCF$_2$ and F ligands are much more favorable. ‘XIIa’, ‘VII’, and ‘VIII’ are energetically the lowest ones, both structurally corresponding to $\text{V}_2\text{O}_5^+ \cdot \text{CF}_3$ ‘VIII’ with an oxygen replaced by a peroxo ligand. The $\text{V}_2\text{O}_6^+ \cdot \text{CF}_3$ complex ‘XIIa’ is an interesting special case because it has a bridging peroxo ligand. ‘XIIa’ is
167 kJ mol$^{-1}$ more favorable than the stablest \( \text{CF}_3 \)-containing isomer, \( \text{III} \). Upon cleavage of the O–O bond, \( \text{XIIa} \) yields \( \text{XV} \), which has a triplet ground state and 95.4 kJ mol$^{-1}$ less stable. \( \text{XV} \) structurally corresponds to \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{XV} \) without methyl group.

### 3.4.3. Formation of \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \)

The abstraction of the CH$_3$ radical from various isomers of \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) can lead to \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) species. The stablist of \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) structures, \( \text{XV} \), yields \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{XV} \). The process requires a \( \Delta E \) of 441.5 kJ mol$^{-1}$, which is even higher than the unsupported CH$_3$–CF$_3$ dissociation. Coupling of two oxygen atoms reduces the reaction energy for the \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{XV} \) to \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) \( \text{XIIa} \) process to 346.1 kJ mol$^{-1}$. Alternatively, the dissociation of \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{VII} \) to form \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) \( \text{XI} \) is exothermic with \( \Delta E = 267.3 \) kJ mol$^{-1}$. The methyl abstraction from \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{XII} \) to give \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) \( \text{VIII} \) has a \( \Delta E \) of 243.4 kJ mol$^{-1}$. The direct formation of \( \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) \( \text{VIII} \) and \( \text{XIIa} \) from its structural precursors \( \text{V}_2\text{O}_6^+\cdot\text{CH}_3\text{CF}_3 \) \( \text{XII} \) and \( \text{XIV} \) has \( \Delta E \) of 203.2 and 215.8 kJ mol$^{-1}$, respectively.

Starting from the free \( \text{V}_2\text{O}_6^+ \) cation, the overall bond cracking process \( \text{V}_2\text{O}_6^+ + \text{CH}_3\text{CF}_3 \rightarrow \text{V}_2\text{O}_6^+\cdot\text{CF}_3 \) \( \text{XVII} \) + CH$_3$ is slightly endothermic (Table 1, reaction 2a).
is $-176.1$ kJ mol$^{-1}$. The reaction should start from a $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ species that contains an intact C–C bond. Thus, the stablest structures of $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ (XII–XV) are not suitable reactants. The possible mechanism for this process includes an internal nucleophilic substitution of oxygen by fluorine in $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ VIII with subsequent or simultaneous dissociation of $\text{CH}_3\text{C(O)}\text{F}$. The reaction energy for the $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ ("VIII") $\rightarrow \text{V}_2\text{O}_4\text{F}_2^+ ("\text{II}"angle + \text{CH}_3\text{C(O)}\text{F}$ is only slightly endothermic with $\Delta E=+30$ kJ mol$^{-1}$. Starting from 'IX', $\Delta E=+108.3$ kJ mol$^{-1}$, though a dissociative mechanism for structures with separated OH ligand is not easily conceivable. When using the stablest $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ cation, 'XIII', the formal dissociation energy is 206.3 kJ mol$^{-1}$.

3.4.6. $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ and $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ cations

In opposite to $\text{V}_2\text{O}_5^+\cdot\text{CF}_3$, the $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ ions were not detected under experimental conditions. Nevertheless, it may be interesting to examine their structure and energetics in order to understand why they are not found. Structurally, $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ species are expected to be rather different from $\text{V}_2\text{O}_5^+\cdot\text{CF}_3$ ones, since the coordination modes of fluorine and hydrogen differ substantially. The structures of $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ cations are shown in Fig. 10. Two of the primary structures ('I' and 'II'), which can be obtained by adding a methyl group to an oxygen of $\text{V}_2\text{O}_5^+$, turned out to be the most stable. The latter structure originates from $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ XII, with the corresponding $\text{CF}_3$ radical dissociation energy $\Delta E=242$ kJ mol$^{-1}$. The secondary structures of $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$, which emerge by a proton transfer from the methyl to one of the oxygens, are 25–42 kJ mol$^{-1}$ higher in energy. The total reaction energy using stablest structures

$\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ ('XIII') $\rightarrow \text{V}_2\text{O}_5^+\cdot\text{CH}_3 ("\text{II}"angle + \text{CF}_3$

is 340.8 kJ mol$^{-1}$ (Table 1), which is only slightly more favorable than the unsupported $\text{CH}_3\text{CF}_3$ dissociation.

The geometry of the $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ cations is considerably different (Fig. 11). Two structures with separated methyl hydrogens and separated oxygens rather than a peroxy ligand are drastically more stable than the other ones, 'VI' (doubly bridged) and 'VII' (singly bridged). Both complexes are coordinatively saturated if we assume that the positive charge is localized at the V2 atoms. The structures 'I', 'III', and 'VIII' with an intact methyl group attached to an oxygen are at least 239 kJ mol$^{-1}$ higher in energy and thus of no importance.

In terms of energetics, the dissociation of the stablest $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$, 'XV', to yield $\text{V}_2\text{O}_5^+\cdot\text{CH}_3$ 'VI' is 201.2 kJ mol$^{-1}$. However, it is obvious that there is no direct pathway between $\text{V}_2\text{O}_5^+\cdot\text{CH}_3\text{CF}_3$ 'XV' and $\text{V}_2\text{O}_5^+$, CH$_3$ 'VI', since this would mean a very dramatic reorganization.

4. Discussion and conclusions

The cations under study, $\text{V}_2\text{O}_5^+(n=5–6)$, have an asymmetric double-bridge structure, (O)$_2$–V–(O)$_2$–V(O) and (O)$_2$(O)–V–(O)$_2$–V(O) in their respective stablest configurations. The $\text{V}_2\text{O}_5^+$ cation has a terminal peroxy ligand. The cations can form weakly bound adducts with CH$_3$CF$_3$ which is connected with fluorine transfer leading to $\text{V}_2\text{O}_5^+\cdot\text{CF}_2\text{CH}_2^\prime$ structures. These adducts can undergo alkyl shift to CH$_3$CF$_2$O(O$_n$–4)V(O)$_2$V(O)F alkoxy structures, which are about 60–100 kJ mol$^{-1}$ more stable. The most favorable configurations are those with separated CH$_3$,
CF$_2$, and fluorine. For V$_2$O$_5^+$·CH$_3$CF$_3$ cation it is a doubly bridged structure, for V$_2$O$_6^-$·CH$_3$CF$_3$ a singly bridged one without peroxo ligands. The formation of both V$_2$O$_5^+$·CH$_3$CF$_3$ from V$_2$O$_6^-$ and free CH$_3$CF$_3$ is very exothermic (reaction 1a, Table 1). The C–C bond cleavage in V$_2$O$_5^+$·CH$_3$CF$_3$ to yield V$_2$O$_5^+$·CF$_3$ and the free methyl radical (reaction 1b in Table 1) is 130 kJ mol$^{-1}$ more energy demanding than the analogous dissociation of V$_2$O$_5^+$·CH$_3$CF$_3$. The total cracking reaction energy (reaction 2a, Table 1) emphasizes the dissimilarity of V$_2$O$_5^+$·CH$_3$CF$_3$ compared to V$_2$O$_5^+$·CF$_3$ cation (reaction 2b; note that 2a and 2b together give the C–C bond cleavage for the CH$_3$CF$_3$ molecule alone).

Another route of the cracking, which would release CF$_3$ (reaction 3 in Table 1) not found in the experiment, is slightly exothermic ($\sim$42 kJ mol$^{-1}$) for V$_2$O$_5^+$, and more exothermic for V$_2$O$_5^+$ ($\sim$137 kJ mol$^{-1}$). One likely reason for this reaction not to occur even for V$_2$O$_5^+$ is that the stabilities of V$_2$O$_5^+$·CH$_3$CF$_3$, ‘XIII’ and ‘XIIIa’ contain an unbroken methyl group (Fig. 3) which can dissociate, while no intact CF$_3$ group is available. The same is true for V$_2$O$_5^+$·CH$_3$CF$_3$ (Fig. 6). In addition, V$_2$O$_5^+$·CH$_3$F$_2$ formation (reaction 3) would lose the competition to V$_2$O$_5^+$·CF$_3$ formation (reaction 2a).

The abstraction of HF from CH$_3$CF$_3$ (reaction 4 in Table 1) is computed to be an exothermic process, with $\Delta E$ of about $\sim$90 kJ mol$^{-1}$ for both V$_2$O$_5^+$·HF and V$_2$O$_6^-$·HF. Thus, the HF abstraction should be approximately equally favorable in the case of V$_2$O$_5^+$·HF. This is in line with the experimental observation of V$_2$O$_5^+$·HF [5].

An important question is the mechanism of the dioxygen dissociation from oxygen-rich cations such as V$_2$O$_6^-$.