Mononuclear metavanadate catalyses gas phase oxidation of methanol to formaldehyde employing dioxygen as the terminal oxidant†

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Multistage mass spectrometry experiments reveal a sequence of gas phase reactions for the oxidation of methanol to formaldehyde with a mononuclear oxo vanadate anion as the catalyst and dioxygen as the terminal oxidant.

Vanadium oxides catalyse a variety of synthetic and industrial oxidation reactions with dioxygen as the terminal oxidant.[1,2] Mononuclear oxo- and peroxo-vanadate centres are active for oxidation of substrates such as alcohols, alkenes, sulfides and halides,[1] while bulk or supported vanadium oxides are employed in the heterogeneous catalytic oxidations of sulfur dioxide to sulfur trioxide, butane to maleic anhydride, and alcohols to aldehydes.[2] Highly dispersed supported vanadium oxide centres retain their activity for the oxidation of methanol, suggesting that only a single metal centre is necessary for catalysis.[2] Recent studies suggest that such sites might involve a vanadium peroxo fragment.[3]

Gas phase studies of ionic transition metal oxides can provide fundamental insights into reactivity and catalytic function under well-defined experimental conditions.[4] A range of oxo-vanadium ions have been studied both experimentally and theoretically.[5,6] Here we provide a preliminary report of multistage mass spectrometry experiments involving ion–molecule reactions and collision induced dissociation that describe a sequence of gas phase reactions for the oxidation of methanol to formaldehyde in which dioxygen is the terminal oxidant and a mononuclear vanadate anion is the catalyst (Fig. 1). Key intermediates are similar in structure to known solution phase catalysts[1] and to supported vanadium oxide centres.[2,3] Such similarity suggests that the intermediates and reactions observed in the present gas phase study might provide insights into these related condensed phase processes.

The oxo-, peroxo- and alkoxo-vanadate(V) anions $[VO_3]^-$, $[VO_2(OH)_2]^-$, $[VO_2(\eta^2\text{-}O_2)]^-$, $[VO_2(OH)(OCH_3)]^-$ and $[VO(\eta^2\text{-}O_2)(OH)(OCH_3)]^-$ are all intermediates in the cycle of Fig. 1. They were generated in the gas phase by electrospray of solutions of $NaVO_3$ in acetonitrile : water or methanol : water which contained hydrogen peroxide.[7] Ground state structures were calculated by density functional theory (DFT), and are included in Fig. 1.‡ Mass
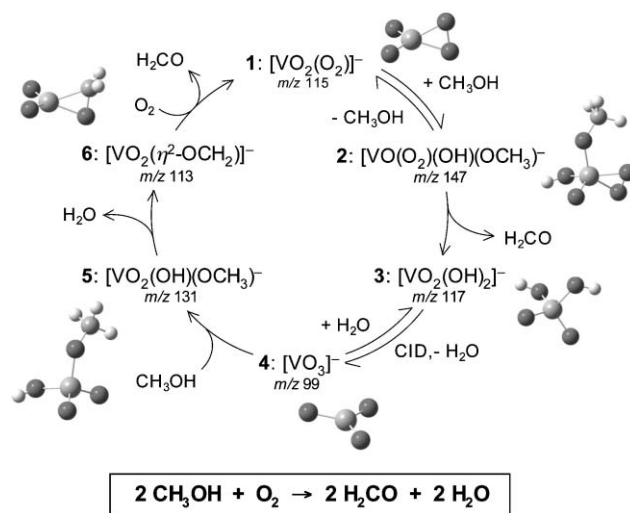

Fig. 1 Gas phase cycle for the oxidation of methanol to formaldehyde, with DFT calculated structures for intermediates **1–6**.

spectra for key ion–molecule reactions and collisional activation experiments are presented in Fig. 2.‡

Mass selection of the dioxo-peroxo anion $[VO_2(\eta^2\text{-}O_2)]^-$ (m/z 115) and reaction with methanol yielded primary product ions at m/z 117 and m/z 147 (Fig. 2a). The product at m/z 117 is assigned to the dioxo-dihydroxo complex $[VO_2(OH)_2]^-$ (**3**) formed *via* formal reduction of the peroxide ligand and oxidative loss of formaldehyde (Fig. 1, **1** → **3**). The product ion at m/z 147 is assigned to the addition complex $[VO(\eta^2\text{-}O_2)(OH)(OCH_3)]^-$ (**2**), which is presumably stabilized by a termolecular collision with helium bath gas. Some of product **3** undergoes further loss of water to produce $[VO_3]^-$ (**4**, m/z 99), which reacts rapidly with methanol to form additional product ions (Figs. 2a, c). The rate of reaction of $[VO_2(\eta^2\text{-}O_2)]^-$ with methanol was measured as 5.3×10^{-11} cm^3 molecule^{-1} s^{-1} (reaction efficiency, $\phi = 0.03$). The reaction to form $[VO_2(OH)_2]^-$ is calculated to be highly exothermic ($\Delta E = -3.54$ eV), indicating that its slow rate must be due to a kinetic barrier. Reaction with CD_3OH resulted in formation of $[VO_2(OH)(OD)]^-$, indicating that the hydroxyl hydrogen and a methyl hydrogen of methanol were retained on product $[VO_2(OH)_2]^-$.[8]

The anion $[VO(\eta^2\text{-}O_2)(OH)(OCH_3)]^-$ (**2**, Fig. 1) is calculated as the minimum energy structure for the addition complex between $[VO_2(\eta^2\text{-}O_2)]^-$ (**1**) and methanol, suggesting that it is likely to be an important intermediate in this reaction. Its collisional activation

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† Electronic supplementary information (ESI) available: Full list of authors for Ref. 18(*a*) and calculated structures and energies for different isomers of $[V, O_3, C, H_2]^-$. See DOI: 10.1039/b612384h
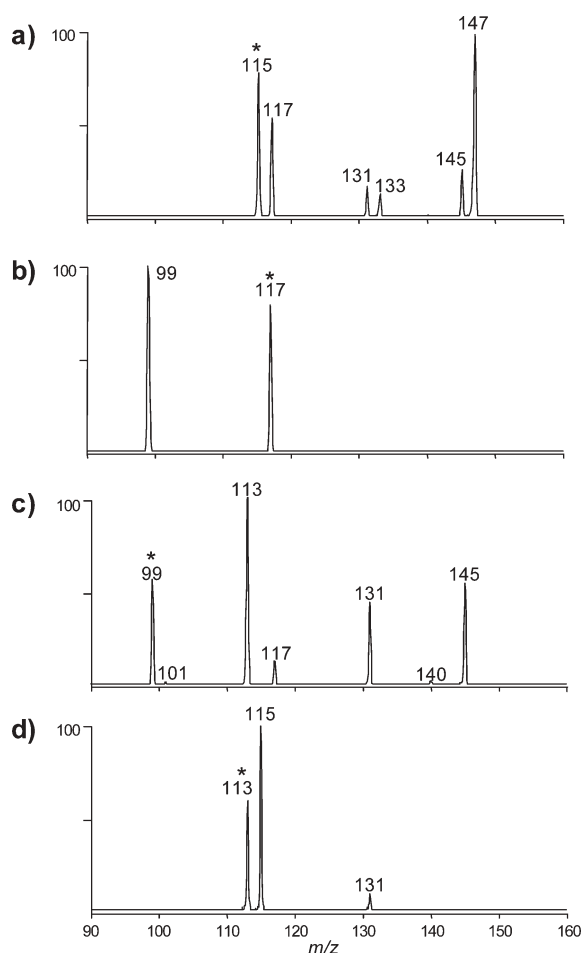
Fig. 2 Mass spectra for the reactions of the catalytic cycle of Fig. 1. The parent ion in each case is labelled with an asterisk, and m/z values for each peak are provided.[8] (a) Reaction of $[VO_2(\eta^2\text{-}O_2)]^-$ (m/z 115, **1**) with CH_3OH to form $[VO_2(OH)_2]^-$ (m/z 117, **3**) and $[VO(\eta^2\text{-}O_2)(OH)(OCH_3)]^-$ (m/z 147, **2**). Some of product $[VO_2(OH)_2]^-$ undergoes loss of water to form $[VO_3]^-$ (m/z 99, **4**), which then reacts rapidly to produce m/z 113 and then m/z 131 and 145 (see (**c**), below). The peak at m/z 133 is due to addition of background H_2O to m/z 115. (b) Collision induced dissociation of $[VO_2(OH)_2]^-$ (m/z 117, **3**) to form $[VO_3]^-$ (m/z 99, **4**). (c) Reaction of $[VO_3]^-$ (m/z 99, **4**) with CH_3OH to form $[V, O_3, H_2]^-$ (m/z 101) and $[VO_2(\eta^2\text{-}OCH_2)]^-$ (m/z 113, **6**). The peaks at m/z 117 and 140 are due to addition of background H_2O and CH_3CN, respectively, to m/z 99. The peaks at m/z 131 and 145 are due to the addition of H_2O and CH_3OH, respectively, to m/z 113. (d) Reaction of $[VO_2(\eta^2\text{-}OCH_2)]^-$ (m/z 113, **6**) with O_2 to form $[VO_2(\eta^2\text{-}O_2)]^-$ (m/z 115, **1**). The peak at m/z 131 is due to addition of background water to m/z 113.

resulted predominantly in the loss of methanol to reform $[VO_2(\eta^2\text{-}O_2)]^-$ (**1**, ~ 97%) and some loss of formaldehyde to form $[VO_2(OH)_2]^-$ (**3**, ~ 3%, data not shown). This behaviour is consistent with **2** being a key intermediate in reaction of $[VO_2(\eta^2\text{-}O_2)]^-$ (**1**) and methanol, but decaying back to reactants in the majority of collisions. The branching ratio to formaldehyde of 3% is in good agreement with the reaction efficiency of $\phi = 0.03$, and suggests that the kinetic barrier in conversion of **1** → **3** is associated with activation of the methoxo ligand in intermediate **2**.

The next step in the cycle of Fig. 1 involves collisional activation of $[VO_2(OH)_2]^-$ (**3**, m/z 117) to eliminate water and form the coordinatively unsaturated metavanadate anion $[VO_3]^-$ (**4**, m/z 99,

Fig. 2b). The reaction is predicted as endothermic ($\Delta E = +2.44$ eV), consistent with it requiring collisional activation to proceed. The reaction is also reversible, with **4** undergoing reaction with background water to reform **3**.

Mass selection and reaction of $[VO_3]^-$ (**4**, m/z 99) with methanol resulted in loss of water to form the major product ion of stoichiometry $[V, O_3, C, H_2]^-$ (**6**, m/z 113, 99%) with a much weaker product ion due to loss of formaldehyde and formation of $[V, O_3, H_2]^-$ (m/z 101, 1%) (Fig. 2c).[8] The rate of reaction was measured as 2.5×10^{-9} molecules cm^{-3} s^{-1}, which is faster than the calculated ion–molecule collision rate of 1.9×10^{-9} molecules cm^{-3} s^{-1} ($\phi = 1.3$).[9] Other ions were also observed due to reaction of $[VO_3]^-$ with background H_2O or CH_3CN, or due to further reaction of product $[V, O_3, C, H_2]^-$ with H_2O or CH_3OH (Fig. 2c).

DFT calculations predicted the lowest energy isomer for product $[V, O_3, C, H_2]^-$ to be singlet $[VO_2(\eta^2\text{-}OCH_2)]^-$ containing a $\eta^2\text{-}C,O$ bound formaldehyde ligand (**6**, Fig. 1). This structure was favoured over other singlet and triplet isomers by at least 0.6 eV (Supporting Information). Calculated metric parameters for $[VO_2(\eta^2\text{-}OCH_2)]^-$ indicate the presence of a $2e^-$-reduced formaldehyde ligand (C–O, 1.39 Å, cf. H_2CO, 1.20 Å and CH_3OH, 1.42 Å at the B3LYP level). Equivalent ligands have been observed experimentally in related condensed phase species, e.g. the vanadocene complex $Cp_2V(\eta^2\text{-}OCH_2)$.[10] The reaction to form $[VO_2(\eta^2\text{-}OCH_2)]^-$ is calculated as exothermic ($\Delta E = -0.42$ eV), consistent with its observation under thermal conditions.

The methoxo-vanadate(v) anion $[VO_2(OH)(OCH_3)]^-$ (**5**, m/z 131, Fig. 1) is calculated as the minimum energy structure for the encounter complex between $[VO_3]^-$ and methanol, suggesting it is likely to be an important intermediate in this reaction. Anion **5** was accessed independently by electrospray of $[VO_3]^-$ in aqueous methanolic solutions, allowing independent examination of its decomposition. Collisional activation resulted in the predominant loss of water (m/z 113, 98%) with only a minor loss of methanol (m/z 99, 2%) (data not shown). The near quantitative conversion of **5** to **6** supports its intermediacy in the reaction of $[VO_3]^-$ with methanol. The observed reaction is consistent with a mechanism involving transfer of a methyl hydrogen to a terminal oxo ligand to form intermediate $[VO(OH)_2(\eta^2\text{-}OCH_2)]^-$,[6c] followed by elimination of water to form $[VO_2(\eta^2\text{-}OCH_2)]^-$.

The 2e-reduced formaldehyde ligand of $[VO_2(\eta^2\text{-}OCH_2)]^-$ (**6**) is formally isoelectronic with peroxide O_2^{2-}, suggesting the possibility of ligand substitution upon reaction with dioxygen. Accordingly, anion **6** reacted with O_2 to eliminate neutral formaldehyde and form a product ion of stoichiometry $[V, O_4]^-$, assigned to the peroxo anion $[VO_2(\eta^2\text{-}O_2)]^-$ (**1**, m/z 115; Fig. 2d). The reaction rate was measured to be 1.5×10^{-11} cm^3 molecule^{-1} s^{-1} ($\phi = 0.03$). The reaction begins on the triplet surface due to the singlet ground state of $[VO_2(\eta^2\text{-}OCH_2)]^-$ and the triplet ground state of dioxygen. It is calculated to be exothermic to yield both singlet and triplet states of product $[VO_2(\eta^2\text{-}O_2)]^-$ ($\Delta E = -1.48$ and -0.61 eV, respectively). The reactivity of product $[VO_2(\eta^2\text{-}O_2)]^-$ is identical to that of authentic singlet $[VO_2(\eta^2\text{-}O_2)]^-$ generated directly by electrospray (same rates and product distributions), indicating that the reaction **6** → **1** involves surface crossing to generate $[VO_2(\eta^2\text{-}O_2)]^-$ in its singlet ground state. The slow rate of reaction is likely due to a kinetic barrier and/or spin bottleneck.[11] The reaction is proposed to proceed by electron transfer from the $2e^-$-reduced formaldehyde

ligand to dioxygen to generate an intermediate ketyl radical anion–superoxide complex, followed by a second electron transfer to generate neutral formaldehyde and $[VO_2(\eta^2\text{-}O_2)]^-$ (**1**) with a peroxo ligand.

The sequence of reactions of Fig. 1 demonstrate a gas phase cycle for the oxidation of methanol to formaldehyde, with a mononuclear oxo-vanadate(V) anion as catalyst and dioxygen as the terminal oxidant. Other gas phase cycles involving O_2 as oxidant have been reported, but these typically involve coordinatively unsaturated metal centres or larger metal clusters.[4,12] In the present case, the mononuclear vanadium centre facilitates $4e^-$ reduction and activation of dioxygen in two stages (Fig. 1): (i) two-electron transfer from the reduced formaldehyde ligand in **6** to dioxygen to form neutral formaldehyde and a peroxo ligand ($H_2CO^{2-} \rightarrow H_2CO + 2e^-/O_2 + 2e^- \rightarrow O_2^{2-}$) and then (ii) intramolecular two-electron oxidation of a methoxo ligand in **2** and concomitant reduction of the peroxo ligand ($H_3CO^- \rightarrow H_2CO + 2e^- + H^+/O_2^{2-} + 2e^- + H^+ \rightarrow O^{2-} + OH^-$). The two steps provide a link between the two-electron oxidation of two molecules of methanol and the overall four-electron reduction of dioxygen to water.

The similarity between important intermediates in the cycle of Fig. 1 and those proposed in heterogeneous and solution phase catalytic applications suggests that the present cycle might provide insights into these processes.[1,2] In particular, the observation of peroxo groups on vanadium oxide surfaces[3,13] suggests that the reactivity of Intermediate **1** (Fig. 1) might be directly relevant to the reactivity of such surface sites. Intermediates containing reduced $\eta^2\text{-}C,O$ formaldehyde ligands equivalent to that in $[VO_2(\eta^2\text{-}OCH_2)]^-$ (**6**) might also be relevant to the interaction of vanadium oxides with methanol, but do not appear to have been considered previously. Collisional activation of $[VO_2(\eta^2\text{-}OCH_2)]^-$ results in decarbonylation to form the dihydride $[VO_2(H)_2]^-$, suggesting the possible role of such intermediates in the over-oxidation of methanol to carbon monoxide. This latter reaction represents the reverse of the reduction of carbon monoxide by metal hydrides, which has been observed previously for related species.[10]

Future studies will include investigation of the reactivity of $[VO_3]^-$ and $[VO_2(\eta^2\text{-}O_2)]^-$ towards other primary, secondary and tertiary alcohols, examination of the heavier congeners $[NbO_3]^-$ and $[TaO_3]^-$,[14] and a more detailed theoretical characterization of the mechanism and potential energy surfaces of the observed reactions.

Notes and references

‡ *Mass Spectrometry*: Experiments were conducted using a modified Finnigan LCQ quadrupole ion trap mass spectrometer equipped with a Finnigan electrospray ionisation source. Electrospray solutions contained $NaVO_3$ (0.1 mg mL^{-1}) in 1 : 1 CH_3CN : H_2O or CH_3OH : H_2O and with the addition of 1% v/v of 30% H_2O_2 solution. The modifications to the mass spectrometer allow for introduction of neutral reagents into the ion trap, allowing the measurement of ion–molecule reaction rate constants. The experimental procedure used for collisional activation and ion–molecule reactions experiments has been described in detail previously.[15] Collision rate constants were determined using the program Colrate.[16]

Theoretical Calculations: Density Functional Theory (DFT) calculations were carried out using the hybrid B3LYP functional[17] with the SDD pseudopotential and associated basis sets for V, and the 6-311++G** basis sets for H, C and O using the Gaussian 03 program.[18a] Stationary points were characterized by frequency calculations, and unscaled zero point energies are included for all species. Structures were visualized using GaussView.[18b]

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