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Vanadium oxide anion cluster reactions with methyl isobutyrate and methyl methacrylate monomer and dimer: a study by FT/ICR mass spectrometry

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Abstract

Laser ablation of vanadium pentoxide (V_2O_5) powder produces VO_3^-, $V_2O_5^-$, $V_3O_7^-$, $V_3O_8^-$, and $V_4O_{10}^-$ cluster ions which have subsequently been reacted with methyl isobutyrate, methyl methacrylate monomer and its dimer in the ion cell region of a Fourier transform ion cyclotron resonance mass spectrometer. Gas phase ion/molecule chemistry has revealed that reactivity decreases with increased mass of the vanadium oxide cluster anions. VO_3^-, $V_2O_5^-$, and $V_3O_7^-$ ions react with the three reagents, methyl isobutyrate, methyl methacrylate and its dimer, respectively, either by addition of a whole reagent molecule or an associated fragment. All products formed are a result of parallel processes. $V_4O_{10}^-$ undergoes no reaction for reaction times of up to 500 s, while $V_3O_8^-$ adds a water molecule. Although the ions possess a net negative charge, the reactive site toward electron rich reagents such as methyl isobutyrate, methyl methacrylate and its dimer is the under-coordinated vanadium atom. This observation is supported by the lack of reactivity toward the studied reagents by those anions ($V_3O_8^-$ and $V_4O_{10}^-$) whose most likely stable structures contain fully coordinated vanadium atoms. (Int J Mass Spectrom 182/183 (1999) 73–84) © 1999 Elsevier Science B.V.

Keywords: Fourier transform ion cyclotron resonance mass spectrometry; Laser ablation; Vanadium oxide cluster anions; Methyl isobutyrate; Methyl methacrylate; Ion-molecule reactions

1. Introduction

Gas phase transition metal and transition metal oxide ion reactions with a variety of organic molecules have been of wide interest and intensively studied with Fourier transform ion cyclotron resonance mass spectrometers (FT/ICR-MS) over the last 20 years [1,2]. This technique has the unique advantage of modeling low concentration situations and solvent free interactions. Low pressure (high vacuum) techniques "expand" the time scale and allow the observation and study of both intermediate and final products of a reaction. Many gas phase ion/molecule reactions have involved the study of monomeric (bare) transition metal and transition metal heteroatom ions [1,3–17]. However, there are fewer studies

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Dedicated to the memory of Professor Ben Freiser. Ben Freiser visited our laboratory at the University of New South Wales in 1986 and, from this meeting as well as other meetings over the following years, he provided us with wonderful encouragement, friendship, and scientific advice. His published works were both intuitive and illuminating and the mass spectrometry community has lost both a great scientist and a friend with his untimely passing.

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of poly(metal) and poly(metal+hetero-atom) cluster reactions in the gas phase [18–29].

Vanadium pentoxide (V_2O_5), in particular, is an important catalyst used in the oxidation of a variety of organic and inorganic molecules, as it is often used as a substrate or support. Catalytic studies on surfaces and, in particular, vanadium oxide surfaces are topical [30,31] and the study of reactivity of metal and metal oxide clusters in gas phase advances our understanding of the catalytic mechanism. Clusters themselves are of particular interest, since for large enough clusters reactivity may model that of bulk material [32,33]. With respect to gas phase reaction investigations, recently Bell et al. [19] have looked at vanadium oxide cation cluster reactivity toward some simple hydrocarbons. Gas phase reactions of some V_xO_y anions with oxygen containing molecules such as methanol and ethanol have been previously reported [34].

Poly(methyl methacrylate) (PMMA) has been continually produced, studied, and commercially used since the 1930s [35]. Free radical polymerization of methyl methacrylate has been the major method used in industry to produce commercial PMMA [36]; however, controlled polymerization processes producing polymers with low molecular weight and/or a narrow polydispersity are currently of interest. Yasuda et al. [37] have used organolanthanide initiators in the production of highly syndiotactic polymers and they show that rare earth metal initiated polymerization gives high molecular weight monodisperse polymers [38]. Other studies have shown that catalytic chain transfer polymerization is an efficient method for the production of low molecular weight poly(methacrylates) [39,40].

The dimer of methyl methacrylate has attracted some attention in the recent literature as it can be used as a chain transfer agent in free radical polymerization reactions [41]. The mechanism of chain transfer to dimer is thought to involve free radical addition to the double bond followed by β-scission. This addition-fragmentation chemistry is seen as a promising route to block copolymers [42]. As well as its importance in chain transfer reactions, the methyl methacrylate dimer can be used as a small molecule analogue of the unsaturated chain-end of a poly(methyl methacrylate) molecule formed by a disproportionation reaction.

The use of mass spectrometry to investigate reactions between metal oxide surfaces (via the metal oxide anion) with the neutral reagent (DMMA) is limited to the observation of processes involving ions and not free radicals; however, there may be parallels between the condensed phase and the gas phase processes [1,43]. The metal oxide cluster anions may provide small surfaces of interaction for the polymer precursor, a first step to polymerization.

Laser ablation has enabled us to produce the VO_3^-, $V_2O_5^-$, $V_3O_7^-$, $V_3O_8^-$, and $V_4O_{10}^-$ clusters. We have studied the reactions of these clusters with methyl methacrylate (MMA) $CH_3OC(O)C(CH_2)CH_3$, methyl isobutyrate (MIB) $CH_3OC(O)CH(CH_3)_2$ (the fully saturated analogue of MMA), and methyl methacrylate dimer (DMMA) $CH_3OC(O)C(CH_2)CH_2C(CH_3)_2C(O)OCH_3$.

2. Experimental

Vanadium pentoxide powder, the methyl isobutyrate, and the methyl methacrylate monomer were purchased from Aldrich. The vanadium pentoxide and the methyl isobutyrate were used as supplied, while the methyl methacrylate was purified by passing it through a column of basic alumina to remove the inhibitor and then dried over calcium hydride.

The methyl methacrylate dimer (DMMA) was synthesized using a catalytic chain transfer polymerization [39] with azobis-isobutyronitrile (AIBN) as initiator and cobaltoxime boron trifluoride as the catalyst. The dimer was isolated in pure form by vacuum distillation using a Kugelrohr unit and its composition and purity confirmed by electron/chemical ionization FT/ICR mass spectrometry.

The laser ablation Fourier transform ion cyclotron resonance mass spectra were obtained using a Spectrospin CMS-47 FT/ICR mass spectrometer equipped with a 4.7 T superconducting magnet [44,45]. The V_2O_5 powder was pressed into a hollowed-out detachable, cylindrical, stainless-steel satellite probe tip. The probe tip was inserted into a titanium single-section

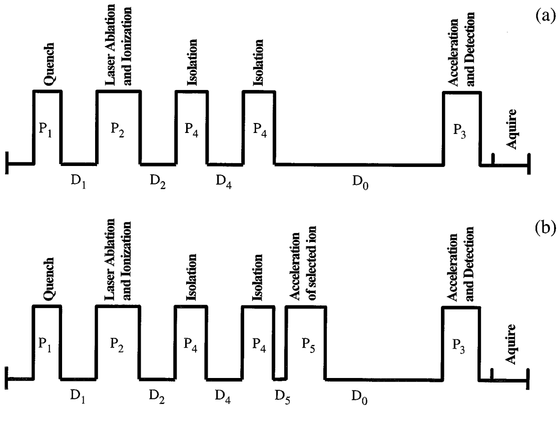

Fig. 1. Pulse sequences for (a) ion/molecule reactions, typically $P_1 = 5\ 000\ \mu$s, $P_2 = 10$ ms, $P_3 = 10\ \mu$s, $P_4 = 40\ \mu$s and $D_0 = 0.0$–100.0 s, $D_1 = 5.0$ s, $D_2 = 0.2$–2.0 s, $D_4 = 1.0$–4.0 s, (b) collision induced dissociation experiments, typically $P_1 = 5\ 000\ \mu$s, $P_2 = 10$ ms, $P_3 = 10\ \mu$s, $P_4 = 40\ \mu$s, $P_5 = 0$–$100\ \mu$s and $D_0 = 0.0$–0.1 s, $D_1 = 5.0$ s, $D_2 = 0.2$–2.0 s, $D_4 = 1.0$–4.0 s, $D_5 = 0.1$ s.

cylindrical ICR cell so that the V_2O_5 surface was at (or close to) the focus of the beam from a Spectra Physics DCR-11 Nd-YAG laser [45]. The background pressure was allowed to stabilize around 2×10^{-9} mbar prior to admission of reagent (MIB, MMA, or DMMA) and Ar cooling gas. The reagent was leaked into the ultra high vacuum (UHV) chamber (using its normal vapor pressure at room temperature) through a Balzers molecular leak valve, and allowed to stabilize at an uncorrected background pressure of 1×10^{-7} mbar. Argon gas was also leaked into the UHV chamber through a second Balzers molecular leak valve, and the gases were allowed to stabilize at a combined total pressure of 3×10^{-7} mbar as measured by a Bayard-Alpert gauge.

The laser ablation experiments were performed with the focused beam (through a lens of focal length 110 mm and spot diameter on the sample of 0.2 mm) of a Nd-YAG laser (1064 nm, 8 ns) at power densities in the range of $P = 0.1$–$20\ 000$ MW cm^{-2}.

A typical event sequence for the laser ablation FT/ICR mass spectrometry experiments is shown in Fig. 1(a). It initially involves a quench pulse $P_1 = 5\ 000\ \mu$s (by inversion of the voltage on one of the trapping plates) followed by a delay $D_1 = 5$ s used to remove from the ICR cell any ions remaining from the previous experiment. The leading edge of a second pulse, $P_2 = 10\ 000\ \mu$s, is used to trigger the 8 ns Nd-YAG laser pulse in the Q-switch mode, after which a delay D_2 (0.2–2.0 s) allows for most of the ablated neutral species to be pumped away, as well for the radiative and collisional “cooling” of the ions trapped in the ICR cell by a combination of magnetic and electric fields. Ion selection is performed (with excitation pulse time of $P_4 = 40\ \mu$s) by using a broad band sweep ejection and single radiofrequency (rf) pulses at selected frequencies, followed by a delay D_4 (1.0–4.0 s) to allow further “cooling” of the ions selected. A second selection of the ions of interest is then performed, after which the ions are allowed to react with the reagent gas for a fixed period of time D_0. This experiment was repeated for reaction times D_0 between 0 and 100 s. After the elapsed reaction time D_0, a 10 μs rf chirp pulse P_3 (135 V applied to each excitation plate 180° out of phase) was used to bring all the ions in the ICR cell into phase-coherent motion, followed by detection of all the ions in the cell and spectra acquisition. Ions were trapped in the cell by potentials applied to the trapping plates in the range of −3.5 to −4.0 V.

Identification of the products of reaction was aided

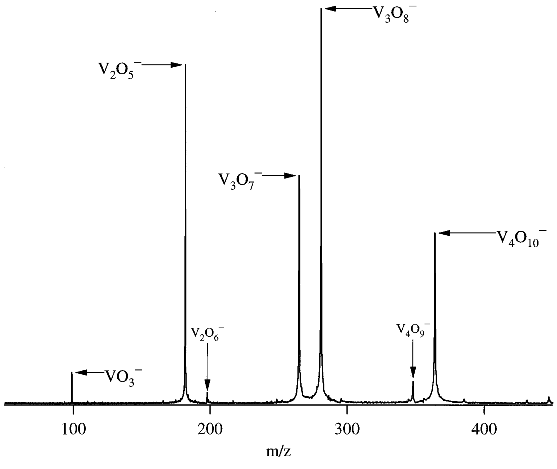

Fig. 2. Negative-ion laser ablation FT/ICR mass spectrum of vanadium pentoxide powder.

Table 1
Product ions for the reactions studied, with their most likely structures. Major products in bold, minor products in plain type

Anion	Products of reaction with methyl isobutyrate	Products of reaction with methyl methacrylate	Products of reaction with methyl methacrylate dimer
VO_3^-	**$[VO_3(CH_3OH)]^-$** **$[VO_3((CH_3)_2CHCH(O))]^-$** $[VO_3(MIB)]^-$	**$[VO_3(CH_3C(CH_2)CH(O))]^-$** **$[VO_3(C_3H_4(CO))]^-$** $[VO_3(MMA)]^-$ $[VO_3(C_3H_4O)]^-$ $[VO_3(CO)]^-$ $[VO_3(H_2O)]^-$	**$[VO_3(DMMA)]^-$** **$[VO_3(CH_3OCH_3)]^-$** $[VO_3(\text{DMMA w/o } CH_3OH)]^-$
$V_2O_5^-$	**$[V_2O_5(MIB)]^-$** $[V_2O_5(CH_3OH)]^-$ $[V_2O_5(H_2O)]^-$	**$[V_2O_5(MMA)]^-$** $[V_2O_5(H_2O)]^-$ $[V_2O_5(C_3H_4O)]^-$	**$[V_2O_5(H_2O)]^-$** **$[V_2O_5(CH_3OCH_3)]^-$** **$[V_2O_5(DMMA)]^-$** $[V_2O_5(CH_3OH)]^-$
$V_3O_7^-$	**$[V_3O_7(MIB)]^-$** $[V_3O_7(MIB)_2]^-$	**$[V_3O_7(MMA)]^-$** $V_3O_8^-$	**$[V_3O_7(DMMA)]^-$** $V_3O_8^-$
$V_3O_8^-$	**$[V_3O_8(H_2O)]^-$** $[V_3O_8(MIB)]^-$	**$[V_3O_8(H_2O)]^-$**	**$[V_3O_8(H_2O)]^-$** $[V_3O_8(CH_3OH)]^-$

by collision induced dissociation (CID) [46,47]. Generation, cooling, and selection of the parent anion were performed, followed by formation of the product ions [see Fig. 1(b)]. The ion of interest was then isolated and accelerated by an rf pulse at the appropriate frequency, of duration P_5 (typically 10–100 μs). After allowing an average of 1–2 collisions of the ions with the Ar atoms to occur, a spectrum was recorded. When the reaction of a vanadium oxide ion with a reagent gas gave multiple major products, MS^n experiments were conducted in an attempt to elucidate pathways of reactions. The anions were also isolated in a background of only Ar gas (at an uncorrected pressure of 2×10^{-7} mbar) to see if any reactions not due to the reagents occurred.

Ab initio density functional theory calculations using Gaussian 94W [48] at B3LYP [49–52] level of theory were used to optimize the structure of the VO_3^- ion. These calculations used a 6-311G basis set with (d, p) polarization functions.

3. Results

Laser ablation of the V_2O_5 sample produced VO_3^-, $V_2O_5^-$, $V_3O_7^-$, $V_3O_8^-$, and $V_4O_{10}^-$ cluster ions (as well as traces of $V_2O_6^-$ and $V_4O_9^-$ ions) and a typical spectrum is shown in Fig. 2. Only the first five anions could reliably be produced and isolated after multiple shots at the same spot on the target, and reactions of each of these anions with each of the three reagents (MIB, MMA, and DMMA) were observed and analyzed. The products of these reactions are shown in Table 1.

VO_3^-, $V_2O_5^-$, and $V_3O_7^-$ all undergo an addition reaction with the reagents to form $[V_xO_y(R)]^-$ complexes, where R is MIB, MMA, or DMMA, respectively, and $(x, y) = (1, 3), (2, 5), \text{ or } (3, 7)$ (see Figs. 3–5). This ion is the major final product in the case of $V_3O_7^-$ (see Fig. 5), while for the other anions a balance between the size of the anion and the reagent molecule controls the abundance of this final product. Figs. 6 and 7 show the reaction profiles of VO_3^- and $V_2O_5^-$ with MIB, MMA, and DMMA, respectively.

The reactions of $V_3O_8^-$ with each of the reagents (MIB, MMA, and DMMA) produce the major product ion $[V_3O_8(H_2O)]^-$ (see Fig. 8). Minor products are also observed: the addition complex $[V_3O_8(MIB)]^-$ for the reaction with methyl isobutyrate and $[V_3O_8(CH_4O)]^-$ for the reaction with methyl methacrylate dimer.

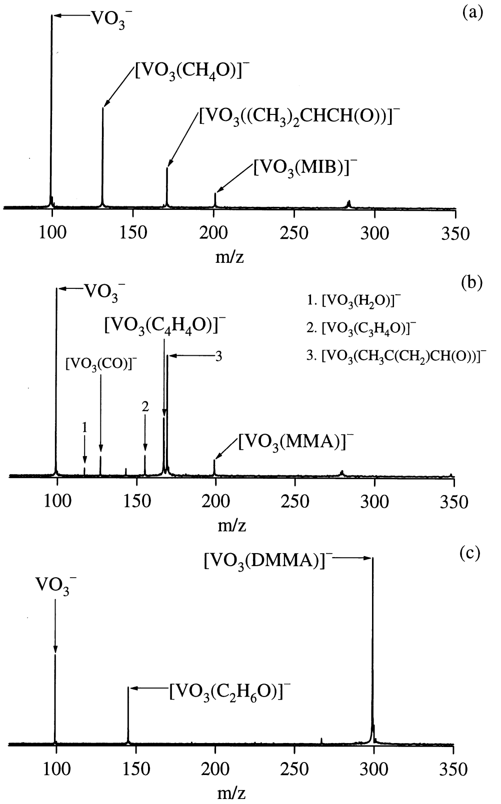

Fig. 3. FT/ICR mass spectra taken after a reaction time of 4 s of the products of VO_3^- reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

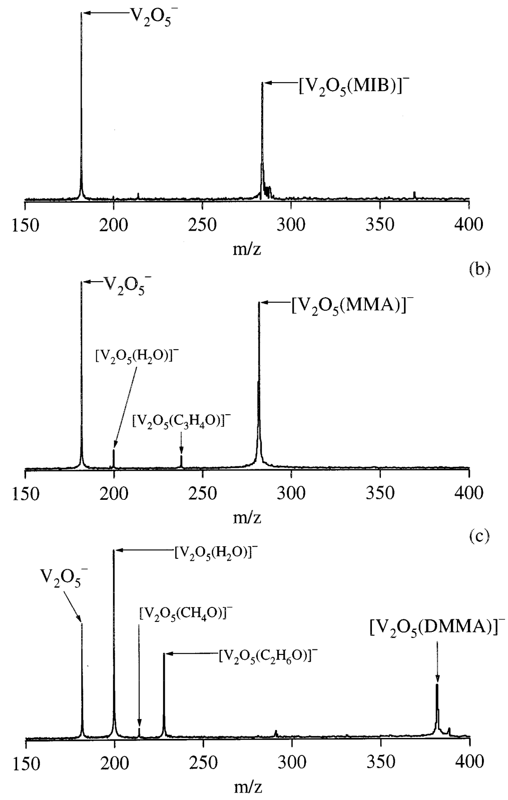

Fig. 4. FT/ICR mass spectra taken after a reaction time of 5 s of the products of $V_2O_5^-$ reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

No reaction products were observed for $V_4O_{10}^-$ with any of the reagents (MIB, MMA, and DMMA), for reaction times of up to 500 s.

Isolation of all the product ions from all the reactions indicate they are all stable to further reaction with MIB, MMA, and DMMA, as well as to dissociation or electron detachment due to collisions. The only indication of a subsequent addition reaction is in the case of $V_3O_7^-$ reacting with methyl isobutyrate, where after long elapsed reaction times a trace of $[V_3O_7(MIB)_2]^-$ is observed. However, this reaction is very slow, and no significant amount of this bis-complex is observed up to 100 s reaction time.

In reactions conducted in the absence of any reagent (only background and Ar gases) each of the anions (with the exception of $V_4O_{10}^-$, which showed no reactivity) underwent an H_2O addition at a rate between 4 and 10 times slower than in reaction with DMMA. No difference in the rate of H_2O addition by the anions was observed for the reactions with MIB and MMA when compared with the reactions in the presence of only background and Ar gases. Positive-ion electron ionization spectra (at 15, 20, 30, and 70 eV) taken at the beginning of each experiment session indicate that while MIB and MMA contained relatively small amounts of water impurities, DMMA contained a much more significant amount (we estimate 1%–2% by volume).

Collision induced dissociation measurements were carried out for all the major product ions. In Figs. 9 and 10 the CID FT/ICR mass spectra of the (a) $[V_xO_y + 46]^-$, and (b) $[V_xO_y$ + reagent molecule$]^-$ adduct products formed in the reactions of VO_3^- and $V_2O_5^-$ with DMMA are presented.

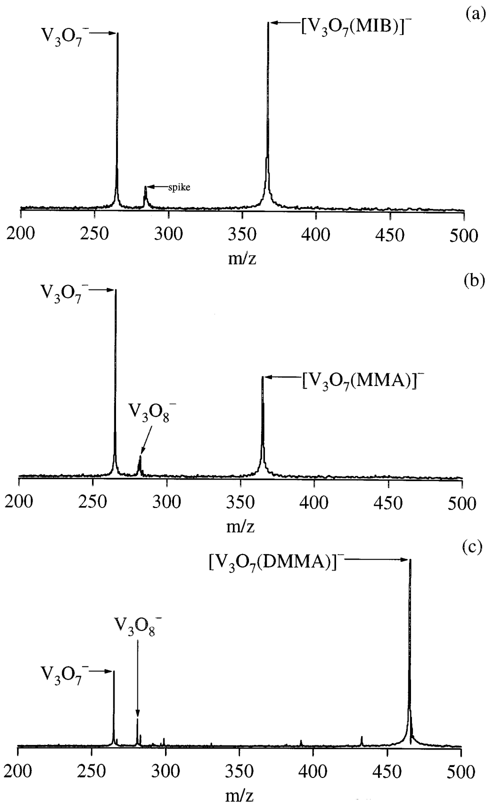

Fig. 5. FT/ICR mass spectra taken after a reaction time of 20 s of the products of $V_3O_7^-$ reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

The optimized structure of the VO_3^- ion* obtained by density functional calculations [Gaussian94W, Becke3LYP with 6-311G(*d,p*) basis set] reveals that this anion has a symmetric trigonal pyramidal structure (V–O = 1.639 *A*°, O–V–O = 117.2°, O–O–V–O = 147.5°), with the vanadium atom retaining a large positive partial charge (+1.45), while the oxygen atoms are equivalent (partial charge −0.82). Preliminary calculations on the $V_2O_5^-$ ion show significant positive partial charges on the vanadium atoms.

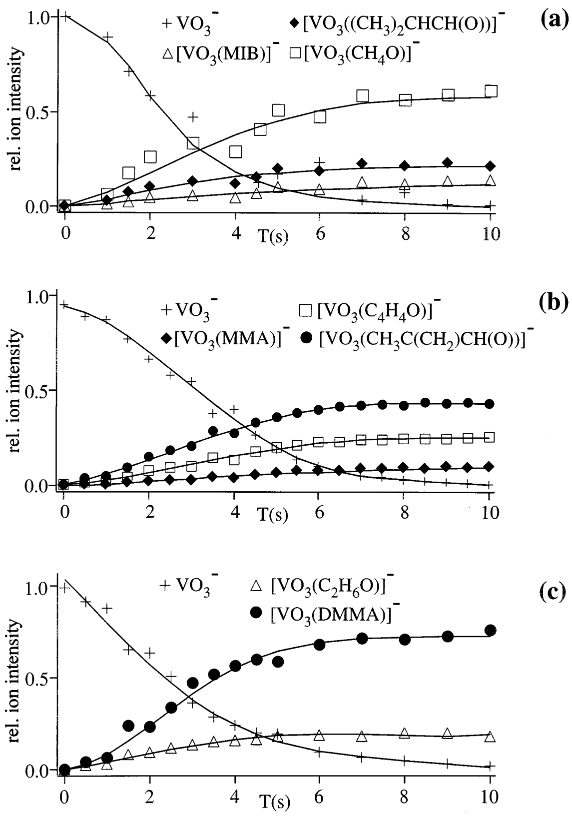

Fig. 6. Reaction profiles of VO_3^- reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

4. Discussion

4.1. Anion reactions

4.1.1. Reactions of VO_3^-

VO_3^- is the smallest and most reactive anion with all three reagents. Reaction profiles are shown in Fig. 6. In the reaction with MIB this ion produces three products as shown in Figs. 3(a) and 6(a), the easiest to identify is the addition product $[VO_3(MIB)]^-$. Although VO_3^- has the highest oxygen/vanadium ratio of the anions studied, the vanadium atom is undercoordinated, and thus exhibits a preference for full coordination by attachment to one of the oxygen atoms present in the reagent molecule. The other two product ions involve bond cleavage:

(a) The addition of CH_4O (most probably CH_3OH)

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* Note: Other groups [55,56] have postulated the structure of VO_3^- to be planar C_{2V}. Our interest in the calculation was primarily to support the claim that the vanadium atom has a large positive charge, which makes it the probable reactive site of the anion.

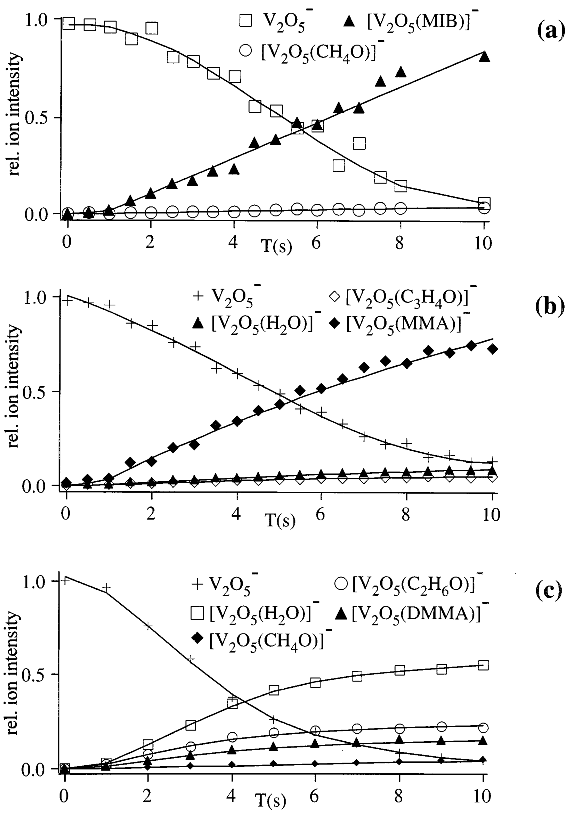

Fig. 7. Reaction profiles of $V_2O_5^-$ reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

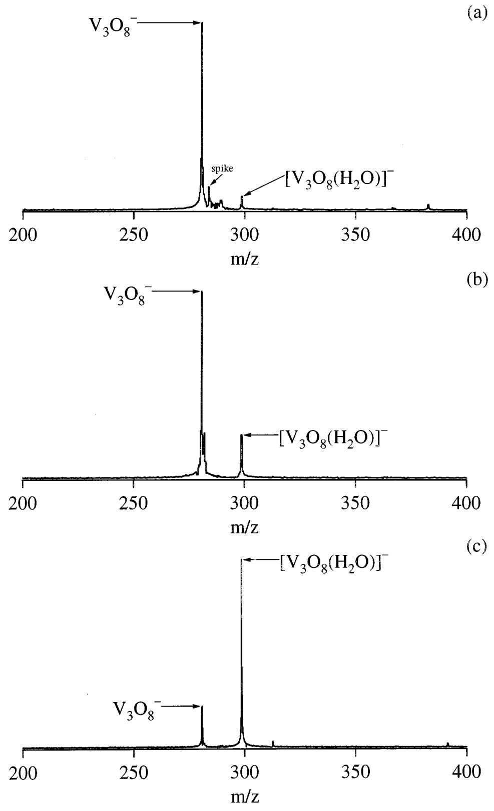

Fig. 8. FT/ICR mass spectra taken after a reaction time of 100 s of the products of $V_3O_8^-$ reaction with (a) methyl isobutyrate, (b) methyl methacrylate, (c) methyl methacrylate dimer.

is accomplished by breaking a C–O bond as well as a C–H bond, and coordination of the vanadium atom of the anion to the methoxy oxygen:

$$VO_3^- + CH_3OC(O)CH(CH_3)_2 \rightarrow [VO_3(CH_4O)]^- + C_4H_6O \quad (1)$$

(b) The loss of CH_2O (most probably formaldehyde) from MIB and coordination to the complementary fragment via the carbonyl oxygen:

$$VO_3^- + CH_3OC(O)CH(CH_3)_2 \rightarrow [VO_3((CH_3)_2CHCH(O))]^- + CH_2O \quad (2)$$

The reaction of VO_3^- with MMA is more complicated, and the products after a reaction time of 4 s are shown in Figs. 3(b) and 6(b). The addition product $[VO_3(MMA)]^-$ is observed, but the major product ions involve loss of CH_2O and CH_4O. The loss of CH_2O is similar to reaction described in Eq. (2); however, the loss of CH_4O suggests attack in the vicinity of the carbonyl oxygen versus attack on the methoxy oxygen as described in Eq. (1), therefore the complementary fragment of CH_4O from MMA coordinates:

$$VO_3^- + CH_3OC(O)C(CH_2)CH_3 \rightarrow [VO_3(C_4H_4O)]^- + CH_4O \quad (3)$$

The preference for the reaction described in Eq. (3) is probably due to the conjugated double bonds in the MMA molecule, and therefore increased electron density in the neighborhood of the C–C bond of the carbonyl and ethylene adjunct carbons. The minor

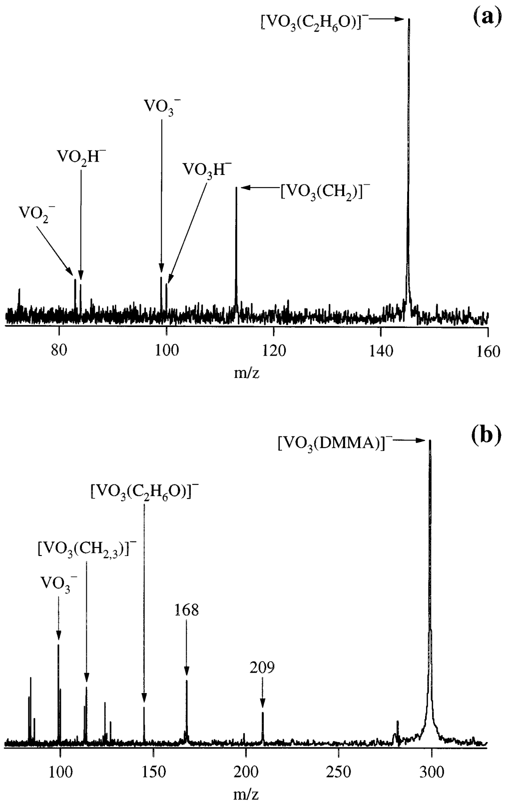

Fig. 9. Collision induced dissociation FT/ICR mass spectra of selected products from reaction of VO_3^- with DMMA: (a) CID of $[VO_3(C_2H_6O)]^-$, (b) CID of $[VO_3(DMMA)]^-$.

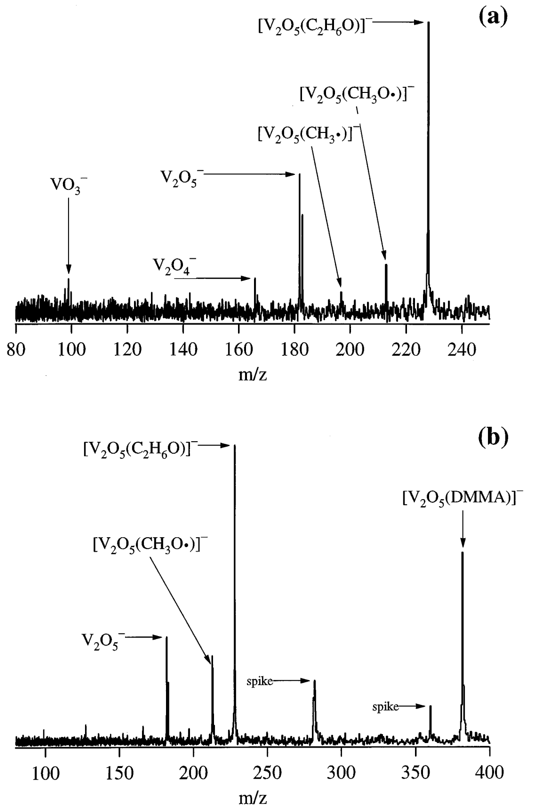

Fig. 10. Collision induced dissociation FT/ICR mass spectra of selected products from reaction of $V_2O_5^-$ with DMMA: (a) CID of $[V_2O_5(C_2H_6O)]^-$, (b) CID of $[V_2O_5(DMMA)]^-$.

products of this reaction involve addition of H_2O, addition of CO, and addition of C_3H_4O, respectively.

The reaction of VO_3^- with DMMA produces only two products as shown in Figs. 3(c) and 6(c): the addition complex, and an ion involving the addition of a species of mass 46 u to the vanadium oxide anion. CID experiments of this ion of $m/z = 145$ [Fig. 9(a)] reveal the cleavage of a neutral of $m/z = 32$ to give the methylene adduct $[VO_3(CH_2)]^-$. Therefore the adduct of $m/z = 46$ is either C_2H_6O or CH_2O_2. The removal of the later molecule from DMMA is unlikely since it requires concomitant breaking of one double bond and at least two single bonds. From previous work [53] the following successive reactions of VO_3^- with methanol are observed:

$$VO_3^- + CH_3OH \rightarrow [VO_3(CH_2)]^- + H_2O \tag{4}$$

$$[VO_3(CH_2)]^- + CH_3OH \rightarrow [VO_3(CH_2)(CH_3OH)]^- \tag{5}$$

These reactions are the result of consecutive interactions with two different methanol molecules. In the reaction with DMMA, VO_3^- is allowed to simultaneously interact with the two methoxy groups present on the reagent molecule, facilitating simultaneous (versus consecutive, as in the reaction with methanol) addition of the two groups, methylene and methanol, via the cyclization of the remaining fragment of the DMMA molecule. Such a reaction is much easier to postulate than extraction of, for example, formic acid from DMMA, and the subsequent rearrangement of the adduct molecule.

Ab initio DFT calculations on VO_3^- [B3LYP with

6-311G(*d*,*p*) basis set] indicate that the partial charge on the vanadium atom is positive and large, and therefore coordination of molecules such as MIB, MMA, and DMMA or oxygen containing fragments of these molecules would occur through oxygen interaction with the vanadium atom, to form addition complexes. Thus coordination of C_2H_6O [most likely $(CH_2)(CH_3OH)$ as discussed above] to the vanadium atom of the anion should also be via an oxygen of this species.

4.1.2. Reactions of $V_2O_5^-$

$V_2O_5^-$ anion is reactive, and in the reaction with MIB the major product is $[V_2O_5(MIB)]^-$, while traces of H_2O and CH_4O addition complexes are also observed [Figs. 4(a) and 7(a)].

The addition complex $[V_2O_5(MMA)]^-$ is the major product for the reaction with MMA, while $[V_2O_5(H_2O)]^-$ and $[V_2O_5(C_3H_4O)]^-$ adducts are two minor products [Figs. 4(b) and 7(b)]. The formation of $[V_2O_5(C_3H_4O)]^-$ is similar to the formation of $[VO_3(C_3H_4O)]^-$ and is unique to these two smaller anions reacting with MMA.

In the reaction of DMMA and $V_2O_5^-$ four products form with the major one being the addition of a water molecule [see Figs. 4(c) and 7(c)]. Unlike in the case for VO_3^-, the adduct anion $[V_2O_5(DMMA)]^-$ is less abundant than the one formed by addition of a C_2H_6O molecule. A trace of $[V_2O_5(CH_4O)]^-$ adduct product is also observed. CID of the ion of $m/z = 228$ ($[V_2O_5(C_2H_6O)]^-$) reveals loss of CH_3, CH_3O, as well as C_2H_6O to give the $V_2O_5^-$ anion, as shown in Fig. 10(a), therefore indicating the composition of this anion to be $[V_2O_5(CH_3OCH_3)]^-$. When $V_2O_5^-$ was reacted with methanol [53] the anion underwent first a methanol molecule addition, then a methylene addition to form a similar final compound as the one described in Eq. (5), and of the same mass as $[V_2O_5(CH_3OCH_3)]^-$. The explanation for the formation of the dimethyl ether adduct is similar to the one for the formation of $[VO_3(CH_2)(CH_3OH)]^-$; however, the CID results are dissimilar. The difference in results between CID of $[VO_3 + 46]^-$ and $[V_2O_5 + 46]^-$ ions is puzzling, and can only be explained by the rearrangement of $[V_2O_5 + 46]^-$ to the dimethyl ether adduct. $[V_2O_5(H)]^-$ does not appear as a product of reaction of $V_2O_5^-$ with DMMA, but it is a CID product of $[V_2O_5 + 46]^-$; this result supports a rearrangement hypothesis.

4.1.3. Reactions of $V_3O_7^-$

$V_3O_7^-$ undergoes the addition of a reagent molecule (MIB, MMA, or DMMA) to form an addition complex as the major product in the case of each reaction, as shown in Fig. 5. Formation of $V_3O_8^-$ is also observed to a small extent in reactions with MMA and DMMA. $V_3O_8^-$ was not observed to form when $V_3O_7^-$ was isolated and trapped in the presence of Ar and background, for up to 100 s. We conclude then that the oxygen atom required to form $V_3O_8^-$ originates from the MMA, or the DMMA molecule, respectively, most likely by abstraction of a methoxy oxygen. Trace amounts of the bis-complex were observed in the reaction with MIB; however, no significant amount of this complex formed after reaction times of up to 100 s. CID experiments on the $[V_3O_7(R)]^-$ complexes (where R is MIB, MMA, or DMMA, respectively) indicate that the complexes are strongly bound. The CID products for $[V_3O_7(MMA)]^-$ are $V_3O_7^-$, $V_3O_8^-$, while for $[V_3O_7(DMMA)]^-$ other fragments of the parent anion are also present.

$V_3O_7^-$ was observed to be much less reactive than VO_3^- and $V_2O_5^-$, as assessed by the rate of disappearance of the parent ion with each of the reagents (MIB, MMA, and DMMA).

4.1.4. Reactions of $V_3O_8^-$

$V_3O_8^-$ reacts to form $[V_3O_8(H_2O)]^-$ with each of the reagents (MIB, MMA, and DMMA). Traces of $[V_3O_8(MIB)]^-$ in the reaction with MIB and $[V_3O_8(CH_4O)]^-$ in the reaction with DMMA are produced (see Fig. 8). A likely stable structure of the $V_3O_8^-$ ion has all the vanadium atoms fully coordinated, thus making any potential positive reactive site (a vanadium atom) unavailable. The anion still has an overall negative charge (although the average electron density per atom is small for such a large ion) allowing the oxygen atoms to coordinate to water hydrogen atoms. The trace amounts of the other observed products indicate that, if reactions between $V_3O_8^-$ and each of the reagents occur, they do so at very slow rates. This result is consistent with the observed decrease in reactivity with increased anion mass. This rate is much slower than the rate of water addition which is not surprising since the attack on the studied reagents from the smaller anions is associated with the undercoordinated vanadium atom. There is also the possibility that various isomers of $V_3O_8^-$ exist in gas phase, each with different reactivity characteristics.

4.1.5. Reactions of $V_4O_{10}^-$

No reaction was observed between $V_4O_{10}^-$ and any of the three reagents (MIB, MMA, and DMMA) for reaction times of up to 500 s. A structure of this anion where the vanadium atoms are fully coordinated would explain the lack of reactivity toward electron rich reagent molecules. Unlike the $V_3O_8^-$ reactions, no addition of water or other molecules was observed. The average charge density per atom on this cluster is smaller than in any of the other clusters. We expect the geometry of $V_4O_{10}^-$ to be similar to that of gaseous P_4O_{10}, where all the possible reactive centers (the vanadium atoms) are sterically hindered [54]. Such a structure, coupled with the small average charge density per atom, could explain the lack of reactivity of this anion toward electron rich molecules.

4.2. General discussion

The three reagents studied, MIB, MMA, and DMMA, are electron rich molecules, both from the presence of oxygen atoms as well as from the C–C double bond in the case of MMA and DMMA. VO_3^-, $V_2O_5^-$, and $V_3O_7^-$ ions, although possessing a net negative charge, most likely react by an attack on either a methoxy or a carbonyl group of the reagent molecule (MIB, MMA, or DMMA). This can be attributed to the existence of a vanadium atom not fully coordinated (all possible structures of these anions involve at least one undercoordinated vanadium atom) as well as to the significantly large positive partial charges on the vanadium atoms (as indicated by the DFT calculations). Discernible trends are the prevalence of the adduct product $[V_xO_y(R)]^-$ with increased anionic mass in reactions with MIB and MMA, whereas no specific trend is observed in reactions with DMMA in this regard.

In the reactions with DMMA, for both VO_3^- and $V_2O_5^-$ the prevalent DMMA fragment addition is that of the postulated $(CH_2)(CH_4O)$ complex. This is probably formed by the initial coordination of the deficient vanadium at one of the methoxy oxygens, followed by the abstraction of a methyl (instead of a hydrogen as in the case of MIB and MMA) probably via the cyclization of the remaining DMMA molecule. No complexes formed with the potentially cyclic complement are observed, which indicates a preference for the methoxy oxygen in DMMA versus the carbonyl group as in the case of MMA.

The $[V_xO_y(R)]^-$ complexes, where R is MIB, MMA, or DMMA, respectively, and $(x, y) = (1, 3)$, $(2, 5)$, and $(3, 7)$, are formed in the reactions of the three smaller studied anions with each of the reagents and are stable when isolated and allowed to undergo further reaction. In the case of VO_3^- reaction with DMMA this complex is the major product, probably due to the small size and structure of the anion, which allows it more coordination freedom. However, in the reactions with MIB and MMA the addition products are minor, which indicates that the V–O bond being formed is stronger than the C–O bond being broken. $V_2O_5^-$ forms as a major product of reaction $[V_2O_5(R)]^-$ with the smaller reagents, MIB and MMA, however, in the reaction with DMMA the addition complex is slightly less likely than the addition of C_2H_6O (most likely dimethyl ether). This opposite trend to the case of VO_3^- could most easily be explained by the existence of different isomers of the anion. Addition of a water molecule is also a product for most of these reactions. From previous work [34], where reactions of these anions with methanol and ethanol were studied, we conclude that the anion-water complex does not come from abstraction of water from the methanol adducts formed. The presence of water as an impurity is the most likely source for the formation of all the anion-water complexes; however, we cannot yet completely discount other pathways.

5. Conclusion

The reactivity of the vanadium oxide cluster anions decreases with increased anion size. For the reactive species, the stable products are formed via one step (no observable intermediates) parallel processes as observed in the reaction profiles presented in Figs. 6 and 7. For reaction times less or equal to 100 s, only in the reaction of $V_3O_7^-$ with methyl isobutyrate is addition of a second molecule to form a bis-complex observed.

Our results indicate that despite the overall negative charge on the vanadium oxide anion (for each of the reactive anions) the center of attack is one of the undercoordinated vanadium atoms. Preliminary ab initio density functional calculations indicate a significantly large positive partial charge on the vanadium atoms, which, coupled with the fact that the reagent molecules are electron rich, makes the attempt at full coordination by the deficient vanadium the most likely reaction path. This is supported by the apparent lack of reactivity of the anions which have all the vanadium atoms fully coordinated.

Because the partial vapor pressure of water is higher than that of methyl methacrylate dimer and ester/water solutions have positive deviations from the ideal, we conclude that the most likely reason for the presence of any of the $[V_xO_y(H_2O)]^-$ complexes is the reaction of the anion with the water present in the UHV chamber [41].

The initial motivation for these studies was to assess whether vanadium oxide anions perform any catalytic function in the polymerization of methyl methacrylates. For the anions studied, no such function was observed; however, the reactions that occurred are interesting and merit attention.

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