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A FOURIER TRANSFORM ICR MASS SPECTROMETRY STUDY OF LASER ABLATED TRANSITION METAL OXIDE ION REACTIONS WITH METHYL METHACRYLATES

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Vanadium oxide ions (VO^+ , VO_3^- , V_2O_5^- , V_3O_7^- , V_3O_8^- , and $\text{V}_4\text{O}_{10}^-$) were generated by laser ablation of pressed oxide powder inside the ICR cell of a FT-ICR Mass Spectrometer. These ions were in turn translationally cooled (in the presence of argon and the reagent gases), isolated, and reacted with methyl methacrylate dimer (DMMA, kept at an uncorrected constant pressure of $\sim 10^{-7}$ mbar). *The elucidation of these reactions forms the subject of this study.*

In order to determine structure of ionic products, collision induced dissociation experiments were performed. To elucidate pathways of the more complicated reactions some of the intermediate products were isolated and allowed to further react with the reagent gas until no further change in product distribution was observed. The vanadium oxide ions were also reacted with methyl methacrylate monomer (MMA) and its saturated analog methyl isobutyrate (MIB).

For the vanadium oxide anions, reactivity toward reagents (DMMA, MMA, and MIB) was observed to decrease with increasing ion mass. For the smaller anions, up to V_3O_7^- , the first products are formed by the anion with a reagent molecule and/or a fragment of it. In Figure 1(a) a summary of the reaction of V_2O_5^- with DMMA is presented as an example. These initial products are stable (no further reactions occur) and indicate, together with results from ab initio quantum chemical calculations, that the under-coordinated vanadium atom is the reactive center. V_3O_8^- anions undergo very slow reactions with addition of one water molecule as the only product observed. $\text{V}_4\text{O}_{10}^-$ was not observed to undergo any reactions for times of up to 1000 s.

VO^+ ions undergo much more complicated reactions than the vanadium oxide anions studied, with the formation of several stages of products. There are two main classes of products: *protonated reagent molecules* and *protonated molecule fragments*, and *VO containing cation adducts* (see Figure 1(b)). In the case of $(\text{MIB}+\text{H})^+$ and $(\text{MMA}+\text{H})^+$ these cations undergo further addition of another reagent molecule to form $[(\text{MIB})_2+\text{H}]^+$ and $[(\text{MMA})_2+\text{H}]^+$ respectively. However, the decay of the VO^+ ion describes a pseudo-first order reaction, which is indicative of a single process responsible for the disappearance of the parent ion. This could be explained by the existence of an intermediate complex which then can follow one of the two paths shown in Figure 1(b).

For the vanadium oxide ions, collision induced dissociation experiments reveal that the anion adducts are more tightly bound than the cation adducts.

We find no evidence of ion mediated polymerization. The dissociation pattern of $[(\text{MMA})_2+\text{H}]^+$ and $(\text{DMMA}+\text{H})^+$ -- two ions of the same mass which arise as products in some of the studied reactions -- are different.

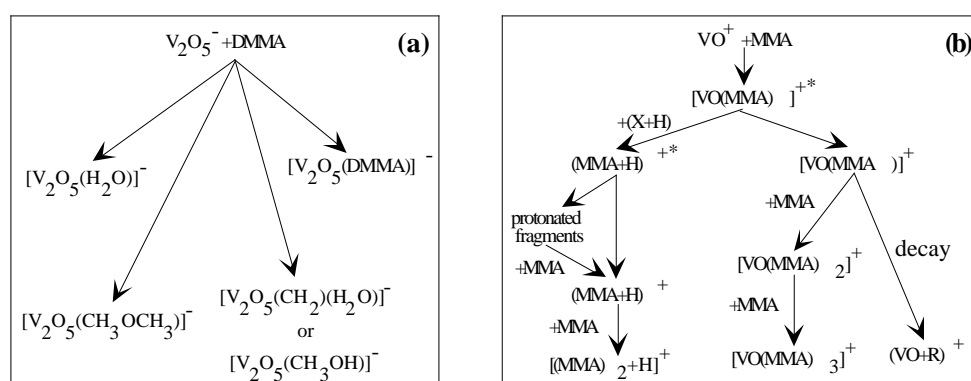


Figure 1. Major reaction pathway schemes for: a) the reaction of V_2O_5^- with methyl methacrylate dimer; b) the reaction of VO^+ with methyl methacrylate monomer (MMA), where R is a fragment of MMA.