

# Synthesis, Structure and Reactivity of Soluble Vanadium Oxides in Organic Media

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Final Seminar

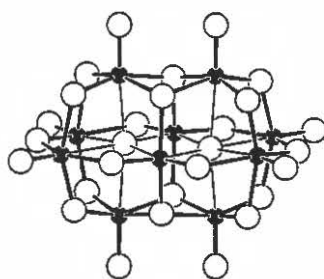
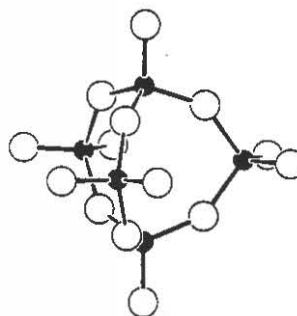
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Traditionally, polyoxovanadates have been prepared in aqueous solution by acidification of the orthovanadate ion  $\text{VO}_4^{3-}$  or by addition of base to  $\text{V}_2\text{O}_5$  [1]. Most of the species present at different solution pH values have been identified [2], their reaction dynamics have been probed [3], and salts of several polyanions such as the  $\text{VO}_4^{3-}$  [4],  $\text{V}_2\text{O}_7^{4-}$  [5],  $\text{V}_{10}\text{O}_{28}^{6-}$  [6],  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$  [7],  $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$  [8],  $(\text{VO}_3^-)_\infty$  [9],  $(\text{V}_3\text{O}_8^-)_\infty$  [10] and  $(\text{V}_5\text{O}_{14}^{3-})_\infty$  [11] ions have been isolated from aqueous solution and structurally characterized in the solid state.

The nonaqueous chemistry of polyoxovanadates is relatively unexplored. It is important to develop this area of vanadium(V) chemistry, because the selective partial oxidation of xylene to phthalic anhydride [12] and butane to maleic anhydride [13] employ  $\text{V}_2\text{O}_5$  on  $\text{TiO}_2$  and  $\beta\text{-(VO)}_2\text{P}_2\text{O}_7$  vanadate catalysts. The focus of the present study was to prepare reactive polyoxovanadates that can serve as starting points for the synthesis of covalent polyoxovanadate derivatives, also species which have structural features normally associated with those present on solid vanadium oxide surfaces. The study of such species is seen as an important step towards identifying and understanding the factors governing the surface reactivity of the solid vanadium oxide catalysts.

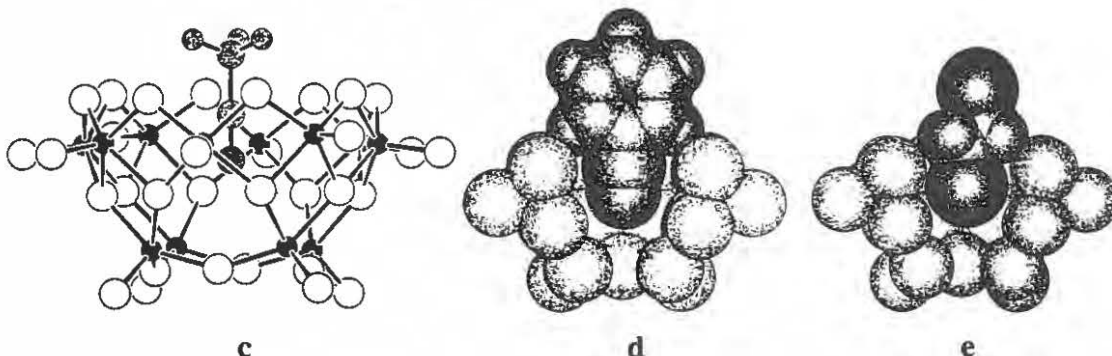
Exploration of the nonaqueous chemistry of polyoxovanadates was initiated by studying the following reaction:  $x\text{H}_3\text{V}_{10}\text{O}_{28}^{3-} + y\text{OH}^- \rightarrow 10\text{H}_n\text{V}_x\text{O}_m^{z-} + (y-n)\text{H}_2\text{O}$  involving the addition of (TBA)(OH) to  $(\text{H}_3\text{V}_{10}\text{O}_{28})(\text{TBA})_3$  in  $\text{CH}_3\text{CN}$ , where TBA = *tera-n*-butylammonium. The first species isolated from this reaction was  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$  **a** as a TBA salt, structural characterization in the solid and solution state reveal that the protonation sites are two  $\text{OV}_2$  oxygens. This anion was found to be unstable in acetonitrile with respect to disproportionation forming two new polyoxovanadates,  $\text{V}_5\text{O}_{14}^{3-}$  [15] and  $\text{V}_{12}\text{O}_{32}^{4-}$  [16]. These are the first unprotonated isopolyvanadates that can be dissolved in aprotic solvents and are thus useful starting materials for the preparation of covalent derivatives.

The structure of the  $\text{V}_5\text{O}_{14}^{3-}$  anion **b** represents a rare example of a transition-metal polyoxoanion cage structure based on corner-sharing of tetrahedral coordination polyhedra, a type of cage structure frequently observed in main group polyoxoanions. According to solution  $^{51}\text{V}$  and  $^{17}\text{O}$  NMR spectroscopy, the  $\text{V}_5\text{O}_{14}^{3-}$  anion is stable in a wide variety of solvents and appears to be reactive towards organic and organometallic reagents [17].

**a****b**

The  $V_{12}O_{32}^{4-}$  anion is formed as an acetonitrile inclusion complex,  $CH_3CN \subset (V_{12}O_{32}^{4-})$ , **c**. Its *nido*- $V_{12}O_{32}^{4-}$  cage framework is a new structure type and can be derived from two different types of *closo*-cage framework previously observed in polyoxovanadate chemistry; the vanadium(V) heteropolyanion  $PV_{14}O_{42}^{9-}$  [18] and the vanadium(IV) anion  $V_{18}O_{42}^{12-}$  [19]. The vanadium coordination geometry within the  $V_{12}O_{32}^{4-}$  cage is similar to that observed in square-pyramidal vanadium(V) compounds such as orthorhombic  $V_2O_5$  [20] and  $\alpha$ - $VOPO_4$  [21]. Moreover, its framework is closely related to the  $V_2O_5$  sheets in the orthorhombic  $V_2O_5$  layer structure.

The  $V_{12}O_{32}^{4-}$  is the first molecular inorganic species known to form inclusion complexes in solution. In an attempt to understand the factors governing the formation and stability of these complexes, synthesis and structural characterization of the  $CH_3NO_2$ ,  $C_6H_5NO_2$ , *p*- $CH_3C_6H_4CN$ ,  $C_6H_5CN$ ,  $NCCH_2CH_2CN$  and 1,2- $CH_2CH_2Cl_2$  host-guest complexes has been achieved. The rigidity of the bowl-shaped structure of the  $V_{12}O_{32}^{4-}$  anion implies shape-selectivity with regard to host binding. Indeed, solution  $^1H$  dynamic NMR spectroscopy studies have shown that binding of  $CH_3CN$  is favored relative to  $C_6H_5CN$  or 1,2- $CH_2CH_2Cl_2$ , and this selectivity is seen to arise from the bulk of the  $-C_6H_5$  and the  $-CH_2Cl$  groups which hinder approach of the guest into the center of the  $V_{12}O_{32}^{4-}$  binding cavity as shown in space-filling models **d** and **e**. The equilibrium constants for host-guest complexation



have been derived, and in some cases enthalpy and entropy of binding have been established quantitatively. Comparison of these parameters with data obtained for cyclophanes [22] and resorcinol based calixarenes [23] is instructive in that it shows behavior analogous to the entire class of purely organic host-guest inclusion chemistry.

The structural analogy between orthorhombic  $V_2O_5$  layers and  $V_{12}O_{32}^{4-}$  host molecules, raises the possibility that this host framework might be capable of affecting C-H activation. It has been already shown that coordinatively unsaturated vanadium sites in vanadates such as  $(VO)_2P_2O_7$  can react with  $CH_3CN$  molecules [24]. The remaining question is whether  $V_{12}O_{32}^{4-}$  can react with saturated hydrocarbons.

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