

Molecular Precursors to Vanadyl Pyrophosphate and Vanadyl Phosphate

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The selective air oxidation of butane to maleic anhydride (MA) is one of the most remarkable examples of heterogeneous, oxidation catalysis. It is a transformation involving $14 e^-$ and seven O atoms and yet is achieved industrially in >60% selectivity at >50% conversion.¹ Catalyst systems have been developed based on using lattice oxygen of vanadium phosphorus species, especially vanadyl pyrophosphate, $(VO)_2P_2O_7$,¹ and vanadyl phosphite, $VO(PO_3)_2$.² The catalysis is generally agreed to be confined to the outermost surface layers of the crystallites. These layers contribute their lattice oxygen atoms to the oxidation and are then regenerated with gas-phase oxygen. This scheme is the basis of the DuPont Co.'s new "riser" reactor technology recently implemented in Asturias, Spain.³ Given the heavy reliance of activity on surface oxidizing power, there has been a continuing interest in developing methods for maximizing the catalyst surface area or depositing the materials onto high surface area supports. Unfortunately, the traditional methods of preparation, involving multiple steps and thermal condensation of insoluble precursor materials,¹ make it difficult to achieve these high surface area species with well defined stoichiometry and phase. Much of the work on supported catalysts for MA production has focused on simple/promoted vanadia species⁴ or on organophosphate treated vanadia where the V:P ratio is variable and the phase identified is $VOPO_4$.⁵ This is a general problem for all but the simplest of metal-oxo species. Borrowing an idea from the semiconductor and MOCVD literature,⁶ we now report two examples of easily prepared, single molecular cluster precursor species. These clusters are highly soluble/processible and are readily decomposed by pyrolysis to yield established vanadium phosphorus phases. The emphasis here is on the cluster synthetic and thermal chemistry; however, we also show that they provide a novel "slosh and burn" route to supported MA catalysts.

Vanadyl(IV) sulfate ($VOSO_4 \cdot 4H_2O$) (0.47 g, 2 mM) in 3 mL of collidine (2,4,6-trimethylpyridine) and 7 mL of methanol is heated under a nitrogen atmosphere. This hot, blue solution is mixed with 5 mL of methanol containing 0.18 g (1 mM) of pyrophosphoric acid, and the clear blue solution is boiled for 5 min and then allowed to cool. Blue crystals deposit directly from this synthesis solution (0.50 g, 85%). X-ray characterization⁷ of the crystals reveals a stoichiometry $(C_8H_{11}NH^+)_4 \cdot (VO)_4(P_2O_7)_2(OCH_3)_4^{4-}$ with structure and key metrics shown in Figure 1a. The cluster anion sits on a crystallographic center of symmetry and contains four, approximately square-pyramidal,

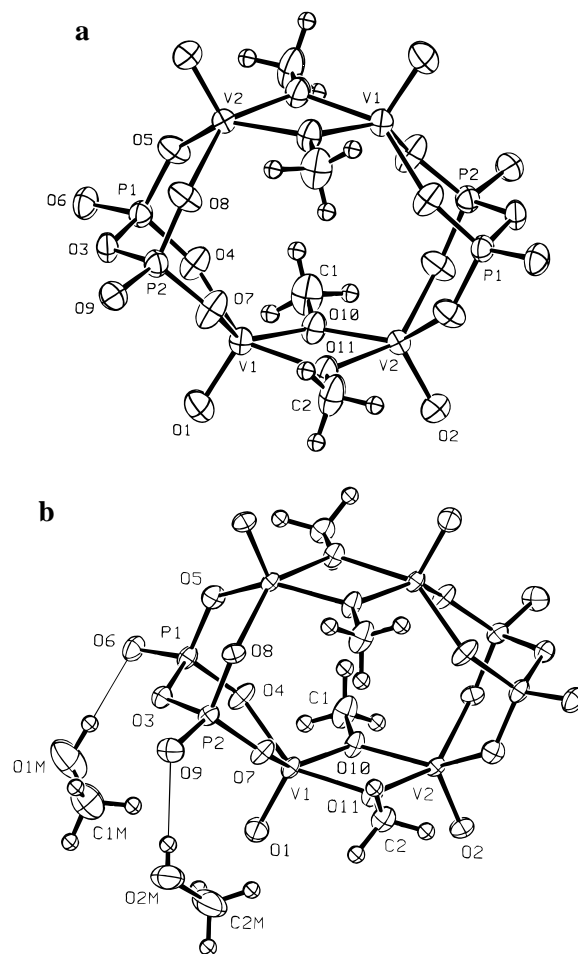


Figure 1. (a) ORTEP drawings of the anion of the cluster salt $(C_8H_{11}NH^+)_4 \cdot (VO)_4(P_2O_7)_2(OCH_3)_4^{4-}$. Selected distances [\AA] and angles [deg]: V–O_{terminal}, 1.589(4); V–O(C)_{av}, 1.97(1); V–O(P)_{av}, 1.95(1); V1···V2, 3.12(2), 4.72(2); V1···V1', 5.31(3); V2···V2', 5.95(3); O1–V1–O(P)_{av}, 108(1); O1–V1–O(C)_{av}, 108.3(4); O2–V2–O(P)_{av}, 106.8(2); O2–V2–O(C)_{av}, 108.4(9); V1–O(C)_{av}–V2, 105.1(5); O10–V_aV–O11, 74.1(3); O(P)–V–O(P)_{av}, 88.7(2); P1–O3–P2, 118.9(2); O4···O10···O8, 124(1). (b) Molecular structure of the cluster anion (showing two of the hydrogen bonded methanols) from the salt with 4 PSH⁺ as the cations. Selected distances [\AA] and angles [°]: V–O_{terminal}, 1.593(4); V–O(C)_{av}, 1.97(1); V–O(P)_{av}, 1.96(1); V1···V2, 3.13(1), 4.51(1); V1···V1', 5.04(2); V2···V2', 5.91(2); O1–V1–O(P)_{av}, 107.8(3); O1–V1–O(C)_{av}, 107.3(5); O2–V2–O(P)_{av}, 106.1(4); O2–V2–O(C)_{av}, 108.4(3); V1–O(C)_{av}–V2, 105.7(2); O10–V_aV–O11, 74.2(3); O(P)–V–O(P)_{av}, 89.3(2); P1–O3–P2, 120.8(2); O4···O10···O8, 132(1).

vanadium(IV) units as two pairs of doubly methoxide bridged dimers. The four vanadyl oxygen atoms radiate from the cluster center. The two dimer units are linked together by intact pyrophosphate groups, each of which is bidentate to each of two different vanadium atoms—one from each dimer pair. The counteranions (collidinium ions) are hydrogen-bonded, one to each of the terminal oxygens of the pyrophosphate groups. It appears that this strong hydrogen bonding leads to very low solubility for this cluster in methanol and all other common organic solvents. Metathesis of the collidinium cations by stirring a slurry of the salt with excess 1,8-bis(dimethylamino)naphthalene (Proton Sponge, PS) in methanol gives a much more soluble compound of which very large, blue, diamond crystals may be grown by evaporation of concentrated methanol solutions (~1 M). Crystal structure analysis⁸ of this material shows that the cluster tetra-anion remains intact with essentially identical metrics, Figure 1b, and even remains sited on a crystallographic center of symmetry. The terminal oxo groups

(1) Vanadyl Pyrophosphate Catalysts *Catalysis Today*; Centi, G. Ed., Elsevier: Amsterdam 1993; Vol. 16. Cavani, F.; Trifirò, F. *Chemtech* **1994**, April. Centi, G.; Trifirò, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Revs.* **1988**, 88, 55.

(2) Sananes, M. T.; Hutchings, G. J.; Volta, J.-C. *J. Chem. Soc., Chem Commun.* **1995**, 243. Sananes, M. T.; Hutchings, G. J.; Volta, J.-C. *J. Catal.* **1995**, 154, 253.

(3) Haggin, J. *Chem. Eng. News* **1995**, April 3, 20.

(4) Michalakos, P. M.; Birkeland, K. E.; Kung, H. H. *J. Catal.* **1996**, 158(1), 349.

(5) Harding, W. D.; Birkeland, K. E.; Kung, H. H. *Catal. Lett.* **1994**, 28(1), 1.

(6) Farneth, W. E.; Herron, N.; Wang, Y. *Chem. Mater.* **1992**, 4, 916.

(7) Pale blue parallelepiped, monoclinic space group $P2_1/n$ with $a = 11.442(4)$, $b = 11.309(3)$, $c = 20.458(6)$ Å, $\beta = 97.80(2)^\circ$ at -55°C , $Z = 2$, $R = 0.043$ for 3323 reflections, $\text{GoF} = 1.07$.

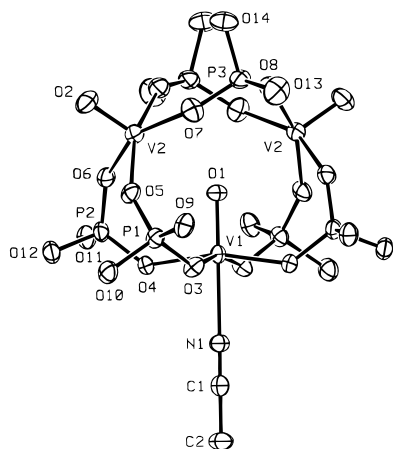
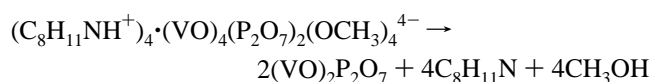


Figure 2. ORTEP drawing of the cyclic trimer $(VO)_3((C_2H_5O)_2PO_2)_6 \cdot CH_3CN$ (the ethyl groups attached to the terminal phosphato oxygen atoms have been omitted for clarity). Selected distances [Å] and angles [deg]: V1–O1, 1.623(4); V2–O2, 1.584(3); O1 \cdots V2, 2.765(3); V1–O(P)_{av}, 1.993(6); V2–O(P)_{av}, 1.98(1); V1–N1, 2.352(6); O1–V1–N1, 180(2); O1–V1–O(P)_{av}, 98.8(9); O2–V2–O(P)_{av}, 102(2); V1–O1 \cdots V2, 125(2); O1 \cdots V2–O2, 177(1).

of the pyrophosphate are now hydrogen-bonded to methanol molecules of crystallization, and the PSH^+ cations are isolated from the anion. (An anion with almost identical connectivity and metrics may also be prepared with methylene diphosphate tetra-anion substituted for the pyrophosphate tetra-anion.) Recognition of the stoichiometry of this cluster immediately suggests that it may be a precursor to $(VO)_2P_2O_7$ itself by simple elimination of 4 equiv of base and 4 equiv of methanol *viz*



Thermogravimetric analysis of the cluster salt confirms this expectation with weight changes expected for the evolution of the collidine and methanol. Weight losses in nitrogen are complete by 500 °C, whereas in air they are complete by ~400 °C. The recovered solid is amorphous (XRD), but on annealing at 700 °C in nitrogen it becomes crystalline with the diffraction pattern of $(VO)_2P_2O_7$ ⁹ (JCPDS card #34-1381).

Diethylphosphoric acid (5.11 g, 3.3 mM) and 2.67 g of vanadyl(V) isopropoxide (1.1 mM) are mixed at 60–90 °C in an open beaker under a nitrogen atmosphere. The mixture becomes a deep blue-green oil from which blue crystals are isolated by dissolution into acetonitrile and layering with hexane. X-ray structure determination of the crystals reveals a material of composition $(VO)_3((C_2H_5O)_2PO_2)_6 \cdot CH_3CN$ as a cyclic trimer (Figure 2).¹⁰ The molecule lies on a crystallographic 2-fold axis. Two of the vanadyl groups point to the exterior of the trimer, while the third points into the center of the ring. This “re-entrant” group exposes a Lewis acid coordination site to the exterior of the trimer where an acetonitrile molecule is N-bonded with a long V–N bond of 2.352 Å. Other common Lewis bases, e.g., THF, will replace the acetonitrile. All of the V in this compound is in the +4 oxidation state indicating that a redox reaction has occurred during its synthesis—the starting compound has vanadium only in the +5 oxidation state. Isopropyl alcohol released during the reaction is the reductant, and the formation of acetone has been confirmed. A structurally

similar complex with benzoate ligands in place of phosphate has been reported previously,¹¹ while the re-entrant oxo motif has also been reported in a pentanuclear oxovanadium organophosphonate.¹²

Thermogravimetric analysis of this complex shows loss of CH_3CN at 80 °C then loss of ethylene, ethanol, water, and diethyl ether with an average overall composition of “ $C_4H_{10}O$ ” at ~300 °C. The final weight (at 500 °C) corresponds to a stoichiometry $VO(PO_3)_2$ and XRD of the recovered material reveals the previously known phase of this material—a known butane to MA oxidation catalyst.²

Both of these highly soluble precursor clusters suggest the potential for use as an entry into novel supported butane oxidation catalysts.⁵ Impregnation onto porous silica (300 m²/g) from concentrated organic solutions of the clusters followed by drying and calcination under conditions (above) designed to produce either $(VO)_2P_2O_7$ (catalyst A) or $VO(PO_3)_2$ (catalyst B) gave high surface area materials (BET of >250 m²/g) loaded with ~10 wt % of the vanadium catalyst phases. XRD analyses of the supported materials show diffraction peaks of the anticipated vanadophosphate phases superimposed on the amorphous silica background. These grey catalyst materials were screened in fixed bed operation for butane to MA oxidation under standard conditions for assessing industrial vanadyl pyrophosphate catalysts (380 °C in a flow of butane:oxygen:nitrogen 2:20:78 at atmospheric pressure). An extensively optimized, pure VPO industrial catalyst gives ~80% selectivity to MA (at 40% conversion of butane) and a MA yield of ~22% (at 0.3 s contact time). Under these same conditions the supported catalysts gave ~30% selectivity and a MA yield of 6% (A) and ~25% selectivity and a MA yield of 2% (B). Clearly, the supported materials are far from competitive with industrial catalysts at this stage of optimization, but they are quite active and if their activity is normalized to a unit weight of V basis, they are 3–5 times more active than VPO itself! The message here is that these cluster species do provide a new route to what are ultimately well defined, both stoichiometrically and in terms of crystalline phase, supported versions of butane to MA catalysts. The challenge remains in refining the catalyst/support interaction or its processing to maximize the selectivity of the catalysis.

The concept of utilizing single molecular clusters as precursors to complex oxide catalyst systems has been demonstrated. The intrinsic processing advantages of such clusters have allowed previously unavailable supported catalysts to be prepared and assessed. These types of clusters may ultimately also provide structural insights into the coordination chemistry of the catalysts and provide clues to favorable structural elements of the heterogeneous catalysts themselves. In favorable cases, these clusters can provide models for studying the reaction chemistry of those structural components and provide some mechanistic clues to the surface chemistry responsible for the catalysis. This has been the subject of our previous publications¹³ and will be a theme of further publications on oxygen sensitive vanadium-phosphato clusters.

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Supporting Information Available: Positional and thermal parameters and crystallographic information and polyhedral structures (10 pages). See any current masthead page for ordering and Internet access instructions.

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(8) Pale blue parallelepiped, monoclinic space group $P2_1/n$ with $a = 14.735(2)$, $b = 15.107(1)$, $c = 22.501(3)$ Å, $\beta = 106.77(1)^\circ$ at -100°C , $Z = 2$, $R = 0.054$ for 5434 reflections, GoF = 1.30.

(9) Bordes, E.; Courtine, P. *J. Catal.* **1979**, *57*, 236.

(10) Bright blue blocks, monoclinic space group $C2/c$ with $a = 24.137(8)$, $b = 16.494(3)$, $c = 14.737(5)$ Å, $\beta = 116.50(1)^\circ$ at -50°C , $Z = 4$, $R = 0.049$ for 3629 reflections, GoF = 2.20.

(11) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3127.

(12) Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 261.

(13) Thorn, D. L.; Harlow, R. L.; Herron, N. *Inorg. Chem.* **1995**, *34*, 2629; Thorn, D. L.; Harlow, R. L.; Herron, N. *Inorg. Chem.* **1996**, *35*, 547.

(14) DuPont contribution 7543.