Phosphatovanadium Chemistry: Behavior of Phosphato Groups Covalently Bound to Only One Vanadyl Center†

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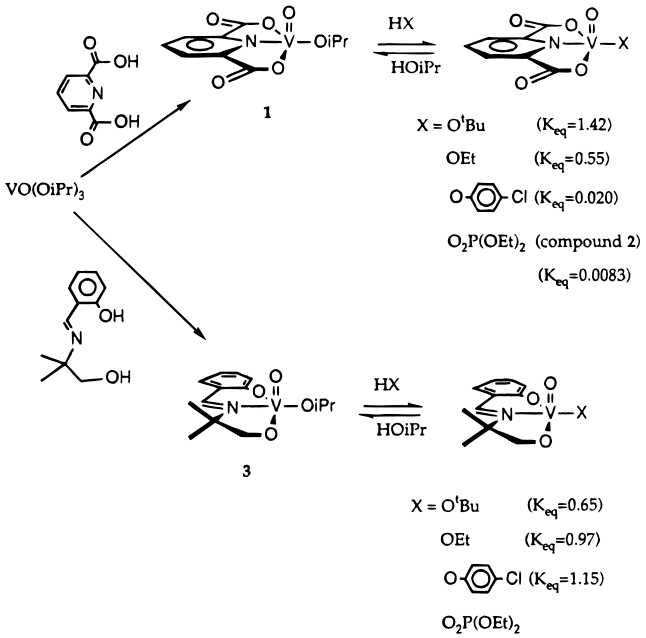
The importance of the "Butox" process (the aireal oxidation of butane to maleic anhydride) and the phosphato−vanadium material ("VPO") that catalyzes it has inspired considerable research into phosphato-vanadium chemistry.[1] But fundamental questions about the coordination chemistry of the vanadium−phosphato bond remain unanswered. The known phosphato−vanadium compounds do not encourage detailed studies of formation and scission of $V-O_{phosphato}$ bonds, owing to difficult characterization of species in solution, complex mechanisms of formation, and/or structures having phosphato groups bridging multiple vanadium centers. Therefore we have found it rewarding to work with a relatively simple vanadium coordination framework that initially has *no* phosphato groups. By determining the necessary conditions for introducing a phosphato group into this framework, we have gained some insight into the underlying chemistry of the phosphato−vanadium bond, which we describe in this article.

The particular framework we employ here is based on "(O,N,O)" supporting ligands. Upon treating a concentrated CH_3CN solution of $VO(O^iPr)_3$ with 1 equiv of pyridine-2,6-dicarboxylic acid ("dipic"), the isopropoxy compound $[(dipic)V(=O)(O^iPr)]_2 \cdot HO^iPr$ (**1**) separates in good yield (see Scheme 1).[2] The essential structure of compound **1**[3] is sketched in Scheme 1. V=O lengths in compound **1** are normal[4] while the V−O^{i}Pr bond lengths (1.750(3), 1.756(3) Å) are somewhat shorter than in the only other V^v−O^{i}Pr structure (1.774(2) Å),[5] a point to which we return later.

In the absence of base,[6] compound **1** undergoes exchange with added alcohols. Selected examples are shown in Scheme 1, with corresponding equilibrium constants.[7] Note that for the (dipic)V(=O) compounds, bulky *tert*-butoxide binds in preference to isopropoxide, which binds in preference to ethoxide. Other hydroxy compounds indicated in Scheme 1 also exchange but compete poorly with simple alcohols; for example, the equilibrium[7] between the diethyl phosphato compound **2** (plus 2-propanol) and the isopropoxy compound **1** (plus diethyl hydrogen phosphate[8]) lies so much in favor of the isopropoxy compound **1** ($K_{eq} = 0.0083$) that the equilibrium concentration of compound **2** is not readily measurable by ^{1}H NMR.

In order to obtain pure diethyl phosphato compound **2** from (dipic)V(=O)(alkoxy) compounds and $HOP(=O)(OEt)_2$ the

Scheme 1



† Contribution No. 7161.

(1) See, e.g.: Thorn, D. L.; Harlow, R. L.; Herron, N. *Inorg. Chem*. **1995**, *34*, 2629−2638 and references therein.

(2) The ethoxy− and *tert*-butoxy−(dipic)vanadyl compounds are described by Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467−475. See also: Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc*. **1986**, *108*, 3711−3718.

(3) Compound **1**, $[(dipic)V(=O)(O^iPr)]_2 \cdot HO^iPr$: monoclinic yellow plates, space group $P2_1/c$, $a = 13.771(4)$ Å, $b = 16.301(6)$ Å, $c = 12.524(4)$ Å, $\beta = 90.00(3)°$ (−100 °C), $Z = 4$, $R = 0.053$, $R_w = 0.041$. Complete details are available as Supporting Information, including a stereo-drawing (Figure S1). The compound exists as weakly-bound dimers in the solid state, where the sixth coordination site of one (dipic)V(=O)(O^{i}Pr) moiety is occupied by a carbonyl group of a second (dipic)V(=O)(O^{i}Pr)(HO^{i}Pr) moiety. In solution the compound appears to be monomeric. ^{1}H NMR (CD_3CN, chemical shifts in ppm downfield from external $SiMe_4$, splitting pattern and coupling constants in parentheses in Hz): 1.67 (d, 6); 6.27 (br sept, 6); 8.21 (d, 8); 8.56 (t, 8); "free" 2-propanol signals at 1.09 (d, 6); 2.45 (br s); 3.86 (sept, 6).

(4) The V=O bond lengths in compound **1** (1.589(3), 1.588(3) Å) are slightly greater than in compound **2** (1.578(2) Å). It is possible that this difference reflects the greater π donation from the isopropoxide in compound **1** than from the diethyl phosphato in compound **2**, but the different groups trans to the oxo also contribute to different V=O bond lengths. See e.g.: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988; Chapter 5. See also: Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1992**, *31*, 3917−3923 and references therein.

(5) Scheidt, W. R. *Inorg. Chem*. **1973**, *12*, 1758−1761. "Oxine" is 8-oxyquinoline.

(6) In the presence of base, e.g. pyridine, compound **1** reacts to form acetone, 2-propanol, and an uncharacterized form of "(dipic)V^{iv}(=O)." The well-characterized related compound (dipic)V^{iv}(=O)$(H_2O)_2$ is known as the water solvate (Bersted, B. H.; Belford, R. L.; Paul, I. C. *Inorg. Chem*. **1968**, *7*, 1557−1562; Sundheim, A.; Mattes, R. *Z. Naturforsch., B*, **1993**, *B48*, 125−132) and as the ethanol solvate (Jones, N. Personal communication).

(7) The indicated exchange reactions reach equilibrium rapidly at room temperature in alcohol or acetonitrile solution. The equilibrium constants included in Scheme 1 are obtained from integrated NMR intensities measured on acetonitrile solutions at 23 °C, and are reported for the general reaction:

$$(ligand)V(=O)(O^iPr) + HX = (ligand)V(=O)(X) + HO^iPr$$

Values are accurate to an estimated ±10% except for the reaction forming (dipic)V(=O)(*p*-chlorophenoxide) where the equilibrium constant is accurate to an estimated ±20%.

(8) We use the term "diethyl hydrogen phosphate" to denote the compound $HOP(=O)(OEt)_2$ even though it is sometimes referred to as "diethylphosphate." To prevent confusion we avoid "diethylphosphate" in this article and instead use the term "diethyl phosphato" to denote the group $-OP(=O)(OEt)_2$.

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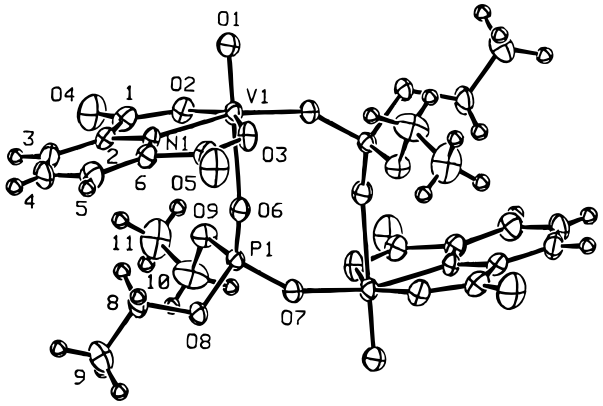

Figure 1. Drawing of the dimer of (dipic)V(═O)(O_2P(OEt)$_2$), compound **2**. Selected bond distances (Å): V(1)−O(1) 1.578(2), V(1)−O(2) 1.905(2), V(1)−O(3) 1.908(2), V(1)−O(7′) 1.869(2), V(1)−N(1) 2.059(3), V(1)−O(6) 2.193(2), P(1)−O(6) 1.484(2), P(1)−O(7) 1.521(2), P(1)−O(8) 1.567(2), P(1)−O(9) 1.561(2). Selected bond angles (deg): O(1)−V(1)−O(2) 94.4(1), O(1)−V(1)−O(3) 95.5(1), O(1)−V(1)−O(7′) 97.3(1), O(1)−V(1)−N(1) 97.6(1), O(1)−V(1)−O(6) 178.4(3).

displaced alcohol must be removed to force the unfavorable equilibrium. This we have accomplished by mixing the methoxy compound (dipic)V(═O)(OMe) (itself obtained by dissolving the isopropoxy compound **1** in methanol[2]) with excess diethyl hydrogen phosphate in toluene and distilling away the methanol. Cooling the concentrated toluene solution thus obtained provided compound **2** as a toluene solvate. The crystal structure of compound **2**[9] is shown in Figure 1; again, dimers are established in the solid state, this time by weak "dative" bonds between phosphato oxygen and the sixth coordination site of the (dipic)V(═O)(O_2P(OEt)$_2$) moiety. The V═O bond length is again normal[4] but the covalent V−$O_{phosphato}$ bond length (1.869(2) Å) is slightly greater than certain other V^v−$O_{phosphato}$ bond lengths (1.849(4), 1.866(4) Å[10]) and much greater than the V−O^{i}Pr bond lengths in compound **1** (1.750(3), 1.756(3) Å). The "dative" V−O(═P) bond of compound **2** (2.193(2) Å) is much longer than other V−phosphato bonds owing to its being trans to the vanadyl oxo atom, an uncommon arrangement[11] imposed here by the planar "(O,N,O)" dipic ligand.

From these observations, we make the following points.

(1) The dipic ligand is not an especially good π donor, so the *"hard acid" (π-accepting) (dipic)(O═)V^{+5} center strives for maximum π-donation from the remaining ligand,* the isopropoxide of compound **1** or the diethyl phosphato of compound **2**. *tert*-Butoxide is a slightly better π donor than isopropoxide, and phenolates, carboxylates, and phosphates are significantly poorer, thus rationalizing the binding order apparent in Scheme 1 and contributing to the difference in lengths between V−$O_{isopropoxy}$ and V−$O_{phosphato}$ bonds.

(2) Following the argument (1) above, *replacing the dipic ligand with another "(O,N,O)" ligand better able to donate π electron density to the vanadyl center should diminish the preference for tertiary alkoxides and make phosphato binding more competitive.* In Scheme 1, we include equilibrium constants for alcohol exchange reactions of the "(O,N,O)" complex (SALAMHP)V(═O)(O^{i}Pr) (compound **3**)[12] and related compounds. The ligand "SALAMHP" provides more π electron density (and steric bulk) to the vanadyl center than does dipic, so π donation from the remaining ligand is less important. Thus binding *tert*-butoxide is now less preferred than binding isopropoxide, which is comparable to binding ethoxide and *p*-chlorophenoxide. In addition, diethyl phosphato binding is readily apparent in NMR spectra of mixtures of compound **3** and diethyl hydrogen phosphate, although rapid exchange prevents quantitative determination of the equilibrium constant.[13] We also note that in the quasi-"(O,N,O)" ligand environment of (oxine)$_2$V(═O)(O^{i}Pr)[5] the V−O^{i}Pr bond length (1.774(2) Å) is slightly greater than those in compound **1** (1.750(3), 1.756(3) Å) as a result of greater π donation from the (oxine)$_2$ ligand environment relative to (dipic).

(3) *The vanadium(+5)−phosphato bond is inherently vulnerable to alcoholysis* (but with equilibrium constants that are determined by the overall coordination environment, as discussed above). This assertion appears to contradict the evidence provided by the portfolio of known phosphato−vanadium dimeric and cluster compounds, many of which were synthesized in alcohol solution,[1] but we note the key aspect **dimeric/cluster compounds.** While single covalent V−$O_{phosphato}$ bonds are vulnerable to alcoholysis, multiply bridging phosphato groups found in most dimers/clusters may resist displacement by alcohols. However, in the high temperature and hydroxyl-rich environment characteristic of the "Butox" process, it is very likely that a significant fraction of surface phosphato−vanadyl bonds are hydrolyzed or alcoholyzed at any given instant and that such alcoholysis/hydrolysis processes are vital to the mechanism(s) of the "Butox" reactions.

Supporting Information Available: Tables of crystallographic information, atomic coordinates, thermal parameters, interatomic distances, and intramolecular angles for compounds **1** and **2** and a stereodrawing of compound **1** (14 pages). Ordering information is given on any current masthead page.

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(9) Compound **2**, (dipic)V(═O)(O_2P(OEt)$_2$)·toluene: monoclinic yellow plates, space group $P2_1/n$, a = 12.343(2) Å, b = 11.922(3) Å, c = 15.122(3) Å, β = 110.91(1)° (−100 °C), z = 4, R = 0.043, R_w = 0.048. Complete details are available as Supporting Information. ^{1}H NMR (CD_3CN): 1.14 (br s); 3.82 (br s); 8.26 (d, 8); 8.62 (t, 8); also, toluene at 2.32 (s); 7.2 (m). {^{1}H}^{31}P (CD_3CN): −8 (br s).

(10) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485−4486.

(11) A pictorial summary of the known types of cyclic (O═V)(OP(R)$_2$O)$_2$-(V═O) bridging units is given by Bond, M. R.; Mokry, L. M.; Otieno, T.; Thompson, J.; Carrano, C. J. *Inorg. Chem.* **1995**, *34*, 1894−1905. Dimeric units having O═V−$O_{phosphato}$ bond angles of essentially 180° (such as appears in compound **2**: 178.4(3)°) were not anticipated.

(12) "H_2SALAMHP" is 2-(salicylideneamino)-2-methyl-1-hydroxypropane. For other vanadium complexes bearing this "(O,N,O)" ligand, see: Carrano, C. J.; Nunn, C. M.; Quan, R.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1990**, *29*, 944−951; Asgedom, G.; Sreedhara, A.; Kivikoski, J.; Valkonen, J.; Rao, C. P. *J. Chem., Soc. Dalton Trans.* **1995**, 2459−2466. ^{1}H NMR data for compound **3** (CD_3CN): 1.29 (s); 1.43 (dd, 6, 1); 1.62 (s); 4.46 (br s); 4.85 (d,10); 5.41 (sept, 6); 6.9 (m); 7.51 (t, 7); 7.60 (d, 7); 8.7 (br s).

(13) Acids are known to catalyze rapid exchange between free alcohol and vanadate ester: White, P. J.; Kaus, M. J.; Edwards, J. O.; Rieger, P. H. *J. Chem. Soc., Chem. Commun.* **1976**, 429−430.