Deoxygenations of $(silox)_3WNO$ and R_3PO by $(silox)_3M$ (M = V, Ta) and $(silox)_3NbL$ (silox = $^tBu_3SiO$): Consequences of Electronic Effects

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Oxygen atom transfers involving terminal metal−oxo functionalities are central to many biological transformations,[1] prominent in applications to organic synthesis,[2−4] and of increasing importance in inorganic systems as synthetic tools,[5−7] objectives in biomimicry,[1,8,9] and targets of fundamental studies.[5−13] As a synthetic route to $(silox)_3WN$ (**4**, silox = $^tBu_3SiO$), the deoxygenation of $(silox)_3WNO$ (**2**) by $(silox)_3Ta$ (**1**-Ta) was attempted without success, despite ample precedent in cleavages of epoxides,[10] N_2O, NO,[11] CO_2, and CO.[12] A comparison study involving sources of $M(silox)_3$ (**1**-M; M = V, Nb, Ta) revealed that features of deoxygenations of **2** and R_3PO (R = Me, Ph, ^{t}Bu) are the consequences of electronic effects enforced by a limiting steric environment.

Table 1. summarizes the deoxygenation studies, and shows that $(silox)_3Ta$ (**1**-Ta) preferred to cyclometalate to $(silox)_2$-$HTaOSi^tBu_2CMe_2CH_2$ (**5**-Ta, 87%, 14 d)[13] rather than deoxygenate $(silox)_3WNO$ (**2**)[14] to $(silox)_3WN$ (**4**, 12%),[14] whereas the smaller $(silox)_3V$ (**1**-V)[14] slowly (85 °C, $\sim 1.4 \times 10^{-4}$ M^{-1} s^{-1}) converted **2** to the nitride. $(silox)_3Nb(\eta^2$-N,C-4-picoline) (**1**-Nb(4-pic), $S = 0$)[11] and $(silox)_3NbPMe_3$ (**1**-$NbPMe_3$, $S = 1$)[14] deoxygenated **2** and formed **4** and $(silox)_3NbO$ (**3**-Nb) swiftly at first, then more slowly as the released 4-picoline and PMe_3 inhibited the reactions, respectively. With a 4-picoline scavenger (**1**-Ta) present in the former, swift cyclometalation to $(silox)_2$-$HNbOSi^tBu_2CMe_2CH_2$ (**5**-Nb, 23 °C, <5 min)[14] competed with deoxygenation; **5**-Nb then slowly deoxygenated **2**, presumably via reversible formation of **1**-Nb. The thermodynamics of deoxygenation[15] were investigated by high-level quantum calculations,[16] with $(HO)_3M$ serving as the model of respective tris-silox centers in **1**-M and **3**-M. In each case the reaction was extremely exoergic (25 °C: M = V, $\Delta G°_{rxn} = -66$ kcal/mol; M = Nb, Ta, −100 kcal/mol). With favorable thermodynamics, the uncompetitive (**1**-Ta) and relatively slow (**1**-V, **1**-Nb) deoxygenations are puzzling.

Since $(silox)_3V$ (**1**-V, $S = 1$) binds various L (L = THF, py, etc.), while $(silox)_3Ta$ (**1**-Ta, $S = 0$) does not,[17] the singlet and triplet states of **1**-M were examined via quantum calculations.[16] Figure 1 reveals that **1**-V is a triplet at the optimized geometries for $S = 0$ ($(d_{z^2})^2$) and $S = 1$ ($(d_{z^2})^1(d_{xz}/d_{yz})^1$), and the T→S barrier is 17 kcal/mol, assuming a facile intersystem crossing. **1**-Ta is a singlet at the optimized $S = 0$ and $S = 1$ geometries and its intersystem crossing barrier is 17 kcal/mol. **1**-Nb is a singlet, but the conversion barrier to a triplet of nearly the same energy is 2 kcal/mol. If the approach of $(silox)_3WNO$ (**2**) to the **1**-M center is linear because of intermolecular silox/silox interactions, then a $4e^-$ repulsion will result in the case of **1**-Ta, but successful docking to an $S = 1$ intermediate $(silox)_3MONW(silox)_3$ (**1**−M−**2**) will occur for M = V, Nb. The additional S−T barrier forced on **1**-Ta allows unimolecular cyclometalation to compete with the bimolecular deoxygenation of **2**.

Table 1 lists the results of R_3PO deoxygenations by (**1**-V, Ta) and **1**-NbL (L = 4-pic, PMe_3), which are predicted by quantum calculations to be exothermic for V (−15 kcal/mol) and Nb or Ta (−45 kcal/mol) with Me_3PO. Curiously, **1**-Ta and **1**-NbL both deoxygenated Me_3PO and Ph_3PO, but failed with $^tBu_3PO$; **1**-Ta cyclometalated to **5**-Ta, **1**-Nb(4-pic) converted to $(silox)_3Nb{=}NCHCHCMeCHCH{=}Nb(silox)_3$ (**6**; 85 °C, 35 d) and 4-picoline,[18] and **1**-$NbPMe_3$ decomposed. The inability to deoxygenate $^tBu_3PO$ is not steric in origin, as an X-ray crystal structure of $(silox)_3V$-OP^tBu_3 (**1**-VOP^tBu_3) attests. R_3PO deoxygenation attempts with **1**-V led to $(silox)_3V$-OPR_3 (**1**-$VOPR_3$; R = Me, Ph, ^{t}Bu),[14] and prolonged thermolysis (100 °C, >20 d) of $(silox)_3VO$ (**3**-V) with PMe_3 afforded some **1**-$VOPMe_3$, consistent with calculations that portray the phospine oxide adducts as the most stable species in the vanadium system.[19,20]

The S−T energetics of Figure 1 do not explain the slow rates of deoxygenation of $(silox)_3WNO$ (**2**) by **1**-NbL and **1**-V, nor do they rationalize the disparate R_3PO (R = Me, Ph) and $^tBu_3PO$ results with **1**-Ta and **1**-NbL. Is there an intrinsic problem to O-atom transfer for **2** and $^tBu_3PO$?

The smaller substrates Me_3PO and Ph_3PO may attack $(silox)_3M$ (**1**-M; M = Nb, Ta) at the side of the PO bond, whereas O-atom transfer from $(silox)_3WNO$ (**2**) and $^tBu_3PO$ may be sterically restricted to occur linearly.[17] With substantial thermodynamic impetus, the deoxygenations are swift as long as $(silox)_3M$-OE

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Table 1. $(silox)_3M$ (**1**-M; M = V, Ta)/$(silox)_3NbL$ (L = 4-pic, PMe_3) + EO → $(silox)_3MO$ (**3**-M) + E and Related Reactions (C_6D_6 or C_7D_8)

$(silox)_3M$/$(silox)_3NbL$ **1**-M; M = V, Ta/**1**-NbL	EO	$(silox)_3MO$ + other products **3**-M; M = V, Nb, Ta	E	*T*(°C)	qualitative rate
1-V	$(silox)_3WNO$ (**2**)	**3**-V	$(silox)_3WN$ (**4**)	85	slow[a]
1-Nb(4-pic)	2	**3**-Nb + 4-pic	4	85	fast then slow[b]
1-$NbPMe_3$	2	**3**-Nb + PMe_3	4	23	fast then slow[c]
1-Nb(4-pic) + **1**-Ta	2	**3**-Nb + **5**-Nb + **1**-Ta(4-pic)	4	23	fast then slow[d]
1-Ta	2	**5**-Ta (87%), **3**-Ta (12%)	**4** (12%)	23[e]	−
1-V	R_3PO (R = Me, Ph, ^{t}Bu)	$(silox)_3VOPR_3$ (**1**-$VOPR_3$)	−	100[f]	−
1-Nb(4-pic)	Me_3PO	**3**-Nb + 4-pic	Me_3P	23	fast
1-Nb(4-pic)	Ph_3PO	**3**-Nb + 4-pic	Ph_3P	23	fast then slow[g]
1-Nb(4-pic)	$^tBu_3PO$	**6**[h]	−	85[h]	−
1-Nb(4-pic) + **1**−Ta	$^tBu_3PO$[i]	**5**-Nb + **1**-Ta(4-pic)	−	23	−
1-$NbPMe_3$	R_3PO (R = Me, Ph)	**3**-Nb + PMe_3	R_3P	23	fast
1-$NbPMe_3$	$^tBu_3PO$[i]	no reaction[j]	−	23	−
1-Ta	R_3PO (R = Me, Ph)	**3**-Ta	R_3P	23	fast
1-Ta	$^tBu_3PO$	**5**-Ta	−	85	−

[a] $k \approx 1.4 \times 10^{-4}$ M^{-1} s^{-1}. [b] Inhibition by released 4-picoline. [c] Inhibition by PMe_3; 61% conversion after 2 d and 86% after 9 d; with 8 equiv of PMe_3, 10% conversion after 2 d. [d] Swift competitive deoxygenation and cyclometalation to **5**-Nb; **5**-Nb then deoxygenates **2** slowly. [e] At 85 °C and 11 h, 23% deoxygenation and 77% **5**-Ta. [f] No deoxygenation after 75 d. For R_3P + **3**-V → **1**−$VOPR_3$: R = Me, 70% conversion after 86 d (100 °C), $k \approx 2 \times 10^{-7}$ M^{-1} s^{-1}. [g] Inhibition by released 4-pic; 50% conversion at $t \approx 0$ and 85% conversion at $t \approx 15$ h. [h] After 35 d at 85 °C, sparingly soluble **6** produced. [i] 10 equiv. [j] Thermal degradation of **1**-$NbPMe_3$ affords multiple products.

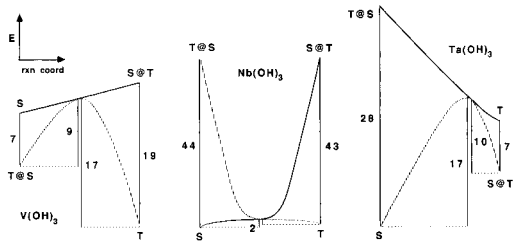

Figure 1. Energetics (kcal/mol, 25 °C) of $(HO)_3M$ (M = V, Nb, Ta) as models for $(silox)_3M$ (M = V, **1**-V; Nb, **1**-Nb; Ta, **1**-Ta). S and T refer to the singlet and triplet energies at those optimized geometries. S@T refers to the singlet energy at the optimized triplet geometry. Intersystem crossing barriers are indicated by the middle vertical lines.

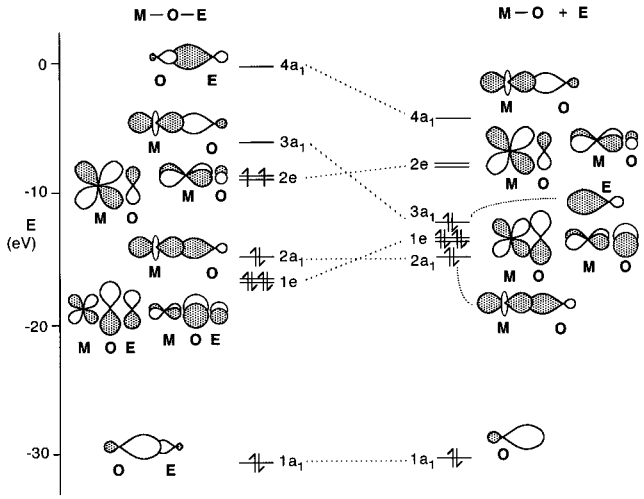

Figure 2. Orbital correlation diagram for generic M-O-E ⇄ MO + E; energetics are based on EHMO calculations of M = $(HO)_3V$. Reactant (*S* = 1) states efficiently intersystem cross to product *S* = 0 states when reactant excited states with populated σ^* orbitals are mixed in effectively; the reduction in symmetry upon bending M-O-E facilitates this process.

(**1**-M-OE, *S* = 1) can be accessed and an additional electronic factor revealed in the molecular orbital diagram in Figure 2 can be overcome. Orbitals of the reactant $^3A_2$ (C_{3v}) $(HO)_3$M-OE complex are shown correlating with the $^1A_1$ product $(HO)_3MO$ + E orbitals. There are only two σ-type orbitals on the reactant—the MO and OE bond pairs—but three on the products; lone pairs on O and E, and the MO σ-bond. Consequently, correlation of a reactant σ^* orbital with a product σ-orbital is required in a linear O-atom transfer, but as the M−O−E angle decreases, σ-character can be mixed into low-lying π-type orbitals. Intersystem crossing must occur at a maximum for a linear O-atom transfer, because significant mixing with an $^1A_1$ excited-state derived from population of the σ^*-orbital is needed to ensure conversion from the $^3A_2$ (reactant) state to the $^1A_1$ (product) state;[21] the greater the degree of bending in the M−O−E angle, the greater the σ/π-mixing, and intersystem crossing becomes more facile.

The mismatch in the numbers of occupied reactant and product σ-orbitals and its effect on intersystem crossing in O-atom transfer are related to several findings: (1) despite a ΔH°_{rxn} of −82 kcal/mol, N_2 scission in $[\{^tBu(3,5\text{-}Me_2C_6H_3)N\}_3Mo](\mu\text{-}N_2)$ has an appreciable barrier ($\Delta H^\ddagger = 23.3$ (3) kcal/mol) and requires a kink in the MoNNMo linkage to facilitate triplet reactant/singlet product intersystem crossing;[22] (2) enantioselective epoxidations using Jacobsen's catalyst require an olefin to approach the Mn(oxo) at a low Mn−O−E angle;[2,3,23] (3) O-atom transfers in bioinorganic systems have been calculated by DFT to occur via transition states with ∠M−O−E near 90°;[24] (4) phosphine oxide chelation may enable the necessary geometry for O-atom transfer;[25] and (5) O-atom transfers from Mn^VO are subject to spin-state crossing effects.[26]

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Supporting Information Available: Spectral and analytical data for all new compounds; experimental procedures; and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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