# Mechanism of Reaction of Reduced Polyoxometalates with O₂ Evaluated by ¹⁷O NMR

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Received August 9, 1996

The reaction of reduced transition metal oxygen anion clusters or polyoxometalates with O₂ (eq 1) is of central importance in many homogeneous and heterogeneous catalytic reactions, some of which have been recently commercialized.[1−11] In addition,

$$POM_{red} + 2H^+ + {}^1/_2 O_2 \rightarrow POM_{ox} + H_2O \qquad (1)$$
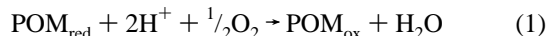
POM = polyoxometalate with reversible redox chemistry

this reaction has been reported in a large number of papers going back to the original work of Matveev who first demonstrated that some reduced heteropolyacids are reversibly oxidized by O₂.[6,11] Despite the ubiquity and importance of eq 1, there is limited information regarding the mechanism of this general process. Mechanisms involving M−O bond cleavage have generally been proposed for aerobic oxidation of POMs in heterogeneous reactions.[2] Two recent studies of O₂ reoxidation of reduced POMs in solution were made, and again, mechanisms involving covalently-bonded M−O intermediates were proposed. In both of the latter studies, oxidation of $[P_2W_{18}O_{62}]^{7-}$ (**2**, 1-electron reduced) in H_2O[12] and $H_{5+x}[PV_2Mo_{10}O_{40}]^{(5+x)-}$ (**3**, *x*-electron reduced, where *x* = 1, 2) in acetonitrile,[13] empirical rate laws were determined and 7-coordinate POM metal centers with M−O bonds, such as terminal and bridging O₂ adducts (generically represented by **A** and **B**, respectively) or an ozonide (**C**), were proposed. Since the energetics of the sterically congested metal centers in **A** and **B** and the weak O−O bond in **C** are unattractive and the rates of eq 1, at least in some systems, are known to be faster than rate of O₂ exchange between H₂O and POM,[14−17] it is curious why an outer sphere (o.s.) mechanism for eq 1, or more precisely one without covalently-bonded M−O intermediates (represented by **D**), is often dismissed. Furthermore, o.s. electron transfer between POMs can be very fast.[18]

Since mechanisms involving covalently-bonded M−O intermediates would lead to O₂ incorporation into the POM competitive with O₂ reduction in eq 1 and an o.s. mechanism, initially,

A   **B**   **C**   **D**
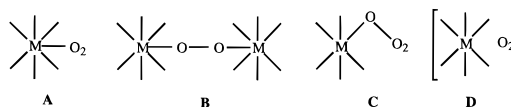
would not, we report here the most direct experiments to date to distinguish these mechanisms. Specifically, the incorporation of ¹⁷O from ¹⁷O₂ during eq 1 and its temporal evolution have been quantified by ¹⁷O NMR for three POM systems, the 2-electron reduced POM $H_2[W_{10}O_{32}]^{4-}$ (**1**), recently characterized in five different protonation states,[19] and **2** and **3** under the literature conditions. This approach and the data below also address the much investigated,[20−22] 2- vs 4-electron O₂ reduction pathways and products (H₂O₂ and H₂O, respectively).

The ¹⁷O NMR spectra were recorded following complete reoxidation of **1** by ¹⁷O₂. All measured peak integrals are corrected for a non-uniform rf power distribution.[19,23] Addition of ¹⁷O₂ at ambient pressure (5 equiv) yields only $H_2{}^{17}O$ (data not shown). At 1.3 atm (10 equiv), however, both H₂O₂ (180 ppm, 39%) and H₂O (−7 ppm, 61%) are produced (Figure 1, see figure captions for experimental details). No peaks attributable to $[W_{10}O_{32}]^{4-}$ are observed.[19] Moreover, 2 equiv of Ph₃P quantitatively reduce the H₂O₂ forming Ph₃PO (49.9 and 47.7 ppm, $^1J_{PO}$ = 149 Hz). The total ¹⁷O product yield (1.01 mM) compares favorably with the theoretical value (10 mM electron equiv = 5 mM O which at 20 atom % ¹⁷O yields 1.00 mM ¹⁷O).

The ¹⁷O NMR spectra recorded both before reduction of α-$[P_2W_{18}O_{62}]^{6-}$ and following complete reoxidation of the 1-electron reduced form **2** by ¹⁷O₂ are shown in Figure 2. The only ¹⁷O-labeled products observed are H₂O₂ and H₂O. As for **1**, the yield of H₂O₂ increases with O₂ pressure and the measured quantities of H₂O₂ and H₂O are in good agreement with the POM reduction equivalents. Importantly, ¹⁷O is not incorporated into the POM framework.

Independent experiments indicate for both **1** and **2** that no ¹⁷O label is incorporated from added $H_2{}^{17}O$ (8.28 atom % ¹⁷O) over the time period of the reoxidations. In addition, the product solutions from eq 1 for both **1** and **2**, containing the oxidized forms of the complexes and $H_2{}^{17}O_2$ (in addition to $H_2{}^{17}O$) were monitored by NMR for 48 h, a time far longer than eq 1 for **2** and 500-fold longer than eq 1 for **1**. No incorporation of ¹⁷O into POM was observed over this longer period. The collective data establish that reaction of H₂O and H₂O₂ with the oxidized forms of the complexes leading to O₂ exchange and likely (but not proven) the same processes for **1** and **2** are far slower than eq 1, and thus, none of these processes interfere with interpretation of the labeling experiments.

Overall, the O₂ oxidation equivalents for both **1** and **2** are reflected quantitatively within the products H₂O and H₂O₂ and no POM enrichment with ¹⁷O is observed whatsoever. All the data are consistent with eq 1 proceeding *via* an o.s. mechanism and not one involving intermediate covalent M−O bond(s). The latter could be ruled out completely if the O₂ exchange chemistry of the hypothetical M−O₂ adduct(s) themselves could be assessed, but there is no evidence for their existence.

In contrast, the case for **3** is not clear as that for **1** or **2**. Here, the simultaneous problems of rapid POM O₂ exchange with $H_2{}^{17}O$, low molecular symmetry, and positional isomerism[24,25] lead to uncertainty in the experimental interpretation. Furthermore, eq 1 for **3** may involve a 4-electron process.[13] The data

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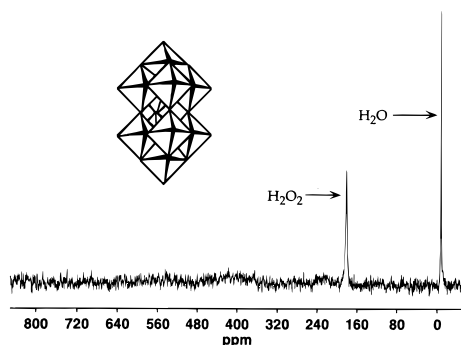(23) Appelman, E. H.; Kostka, A. G.; Sullivan, J. C. *Inorg. Chem.* **1988**, *27*, 2002.

Figure 1. ^{17}O NMR spectrum (67.82 MHz) of $H_2[W_{10}O_{32}]^{4-}$ (**1**, 5 mM in CH_3CN) and $^{17}O_2$ (20 atom % ^{17}O; 10 equiv per equiv of **1**; initial total pressure ~1.3 atm) in 2 mL of CH_3CN following complete oxidation (~5 min). The screw-cap NMR tubes used (5 in. long; 10 mm o.d.) were sealed with silicone/PTFE liners. The spectrum was recorded without either sample spinning or locking, and it was referenced externally to 50:50 H_2O/D_2O. A spectrum recorded prior to $^{17}O_2$ addition and under otherwise identical conditions exhibited no ^{17}O NMR signals. A fully-resolved spectrum of $[W_{10}O_{32}]^{4-}$ and general procedures for obtaining high-quality ^{17}O NMR spectra of polyoxometalates at natural ^{17}O abundance are reported elsewhere.[19]
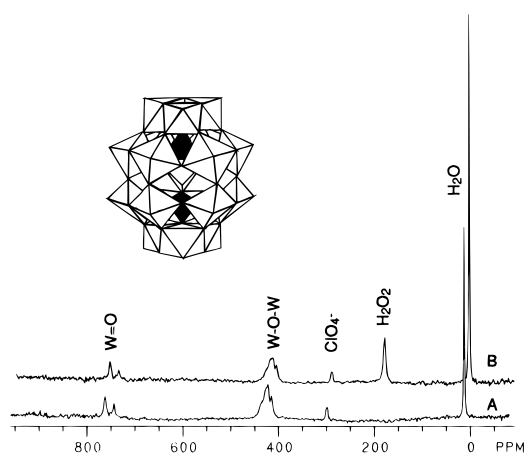

Figure 2. ^{17}O NMR spectra (67.82 MHz) stack plot recorded both before and after the reoxidation of α-$[P_2W_{18}O_{62}]^{7-}$ (**2**) by $^{17}O_2$. A. Spectrum (offset from B) of pH 2.04 aqueous solution (^{17}O-depleted H_2O, <0.01 atom % ^{17}O) of α-$[P_2W_{18}O_{62}]^{6-}$ (0.2 M) and 2-propanol (0.1 M). POM solubility enhanced by addition of $NaClO_4$ (6 equiv) followed by filtration of $KClO_4$ precipitate. B. Spectrum of the same sample after photochemical reduction (9 h irradiation with medium-pressure 500 W Hg lamp; $\lambda > 280$ nm) and then complete reoxidation by $^{17}O_2$ (20 atom %; 0.9 equiv per equiv of POM; 12 h at 55 °C).

do, however, point to a similar mechanism: (1) Figure 3 shows an ^{17}O NMR stack plot for the reoxidation of **3** by $^{17}O_2$. After 11.5 h (82% reaction), the $H_2{}^{17}O$ signal increases 21-fold (representing 94% of all ^{17}O products) via zero-order growth kinetics consistent with limiting mass transfer ($k_{obsd} = 2.1 \times 10^{-7}$ M s^{-1}; Figure 1S, Supporting Information); whereas, the total POM enrichment increases only 2-fold (representing 6% of all ^{17}O products, 3.4% Mo$-^{17}O-$Mo and 2.8% Mo$=^{17}O$). After 33 h (96% reaction), the ^{17}O products are 86% $H_2{}^{17}O$, 8% Mo$-^{17}O-$Mo and 6% Mo$=^{17}O$. The peaks originating from Mo$-$O$-$V, V$-$O$-$V, or V$-$O are not observed. (2) The rate constant of POM ^{17}O enrichment in **3** during reoxidation is identical within experimental error to that measured for exchange between $H_5[PV_2Mo_{10}O_{40}]$ and $H_2{}^{17}O$. These rates were assessed by integrating over the resonances of a given class (*i.e.*, Mo$-$O$-$Mo or Mo$=$O) and thus represent ensemble

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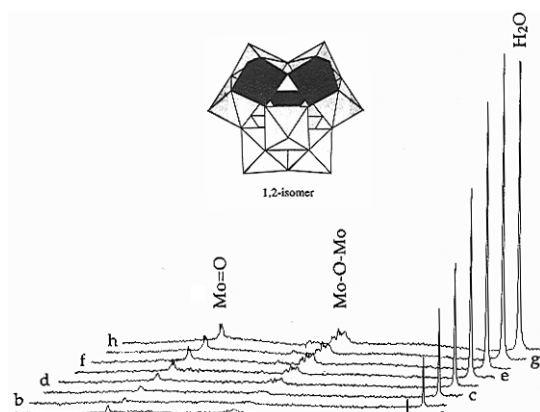(25) Pettersson, L.; Andersson, I.; Selling, A. *Inorg. Chem.* **1994**, *33*, 982.

Figure 3. Stack plot of time-dependent ^{17}O NMR spectra (67.82 MHz) recorded both prior to and during the reoxidation of 0.052 M **3**): (a) *before* addition of 1,3-cyclohexadiene; (b) *after* adding both 1,3-cyclohexadiene (5 equiv)[13] and $^{17}O_2$ (20 atom %; 0.5 equiv per equiv of **3**; initial total pressure ~1.15 atm) at $t = 0.6$ h; (c) 1.9 h; (d) 3.6 h; (e) 6.4 h; (f) 9.2 h; (g) 12.0 h; (h) 33.4 h. Each spectrum was averaged with 100 000 scans (~34 min/spectrum).

averages of the different oxygens within a class. Both the Mo$-$O$-$Mo and Mo$=$O ensembles exhibit a first-order kinetics growth where $k_{obsd} = 2.6 \pm 0.2 \times 10^{-5}$ s^{-1} for Mo$=^{17}O$. For comparison, an $H_2{}^{17}O$ exchange experiment (0.052 M $H_5[PV_2Mo_{10}O_{40}]$ in CH_3CN, 8.28 atom % $H_2{}^{17}O$ at 0.5 equiv per equiv of $H_5[PV_2Mo_{10}O_{40}]$) exhibits first-order kinetics for enrichment of the POM with $k_{obsd} = 2.7 \pm 0.1 \times 10^{-5}$ s^{-1} for Mo$=^{17}O$ (Figures 2S and 3S, Supporting Information) and $k_{obsd} = 2.7 \pm 0.5 \times 10^{-5}$ s^{-1} for Mo$-^{17}O-$Mo. These rates can be compared, since nearly all the $^{17}O_2$ is converted to $H_2{}^{17}O$ before any ^{17}O incorporation into POM is observed. In other words, the kinetically dominant reaction for label incorporation in both cases is $H_5[PV_2Mo_{10}O_{40}]$ + $H_2{}^{17}O$. Furthermore, from isotope exchange kinetics, the ^{17}O concentration dependence of the rate for reaction of POM and $H_2{}^{17}O$ will be a constant: $[POM]_{total}$ $[H_2O]_{total}/([POM]_{total} + [H_2O]_{total})$, where $[POM]_{total}$ and $[H_2O]_{total}$ represent the concentrations of unlabeled plus ^{17}O-labeled POM and H_2O, respectively.[26] The identical rate constants provide strong albeit indirect evidence that the ^{17}O incorporation observed during the redox reaction originates from $H_2{}^{17}O$ rather than from $^{17}O_2$ or an intermediate en route to $H_2{}^{17}O$. (3) The rate constant for ^{17}O incorporation from $H_2{}^{17}O$, k_1 in eq 2, based on the NMR measurements is sufficiently slow that mechanisms involving rapid ^{17}O incorporation into **3** via M$-$O intermediates followed by wash out of the label to the observed levels can be ruled out. Since the equilibrium constant, $K = k_1/k_{-1}$ for eq 2 is ~1.0, the label wash out rates k_{-1} must also be sufficiently slow that any label incorporation into POM during the redox process (eq 1) should be detectable under our conditions.

$$POM + H_2O* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} POM* + H_2O \qquad (2)$$

In conclusion, the experimental evidence here suggests that an o.s. mechanism for reaction of O_2 with reduced polyoxometalates not only warrants consideration but may well be the dominant mechanism for this generic process.

Supporting Information Available: Kinetics plots for reoxidation of **3** by $^{17}O_2$ ($H_2{}^{17}O$ and Mo$=^{17}O$ growth) and exchange with $H_2{}^{17}O$ (Mo$=^{17}O$ growth); an ^{17}O NMR stack plot of the $H_2{}^{17}O$ exchange with $H_5[PV_2Mo_{10}O_{40}]$ (4 pages). See any current masthead page for ordering and Internet access instructions.

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