the core oxidation state assignment $\{V^{III}(\mu\text{-}N)V^{IV}\}^{4+}$. Ongoing studies are directed toward exploring the magnetic properties, reactivity of the nitride group and substitution of the nonbridging ligands in **1**.

Supplementary Material Available: A fully labeled ORTEP drawing and tables of crystallographic data, positional and isotropic thermal param-eters, anisotropic thermal parameters, interatomic distances, and inter-atomic angles (9 pages); a table of structure factors (64 pages). Ordering information is given on any current masthead page.

Department of Chemistry   **David B. Sable**
University of California   **William H. Armstrong***
Berkeley, California 94720

Articles

Contribution from the Institute of Physical Chemistry,
NCSR Demokritos, 153-10 Athens, Greece

Photocatalytic Oxidation of Organic Compounds by Polyoxometalates of Molybdenum and Tungsten. Catalyst Regeneration by Dioxygen

A. Hiskia and E. Papaconstantinou*

Catalyst regeneration (reoxidation) is key to the effective photocatalytic oxidation of a variety of organic compounds by poly-oxometalates. This paper reports on the reoxidation mechanism of photoreduced polyoxometalates by dioxygen. The overall general reaction, presented generally as $M^{(n+1)-} + \frac{1}{4}O_2 + H^+ \rightarrow M^{n-} + \frac{1}{2}H_2O$ [where $M^{n-} = P_2W_{18}O_{62}{}^{6-}$ ($P_2W_{18}{}^{6-}$), $SiW_{12}O_{40}{}^{4-}$ ($SiW_{12}{}^{4-}$), $H_2W_{12}O_{40}{}^{6-}$ ($H_2W_{12}{}^{6-}$)], appears to be first order with respect to polyoxometalates and oxygen and zero order with respect to H^+ at pH <1.5 and pH >3. At the inflection point, the order with respect to H^+, is 1.1 ± 0.4. Rate constants at low pH are 3.8×10^{-3}, 1.0, and >5.5 s^{-1} and at high pH are 0.0, 2.7×10^{-2}, and 0.15 s^{-1} for $P_2W_{18}{}^{7-}$, $SiW_{12}{}^{5-}$, and $H_2W_{12}{}^{7-}$, respectively (Figure 3). Reoxidation of molybdates is known to be considerably slower; $P_2Mo_{18}{}^{8-}$ is not reoxidized by dioxygen, whereas $P_2Mo_{18}{}^{10-}$ reoxidation is from 4 to more than 6 times slower than that of the polyoxotungstates in acid solution. As previously shown with the molybdates, the rates are a function of the degree of reduction; for instance, the rate constants for doubly reduced $P_2W_{18}{}^{8-}$ are about 5 times larger than those for the corresponding singly reduced $P_2W_{18}{}^{7-}$ anions under identical conditions. The rates parallel the redox potential of the polyoxometalates. Limited work was also done with hydrogen peroxide, which seems to behave differently from dioxygen; the results are compared.

Introduction

There has been considerable growth in understanding the catalytic action of polyoxometalates in the last 10 years.[1] Im-portant industrial applications such as oxidation of unsaturated aldehydes or methacrolein or the hydration of propene or isobutene etc. use polyoxometalates as catalysts.[2]

The photocatalytic action of these compounds has been dem-onstrated for the oxidation of a variety of organic compounds. It has been shown that polyoxometalates undergo multielectron photoreduction in the near-visible and UV regions, in the presence of a variety of organic compounds, with concomitant oxidation of the organic compound. Quantum yields of 10–20% have been obtained for the oxidation of alcohols,[3a] whereas smaller quantum yields have been obtained for other organic compounds;[3b] Hill and Renneke, though, have reported 100% quantum yields for pho-toreduction of $W_{10}O_{32}{}^{4-}$ in the presence of cyclooctane in acid solution.[3c]

Recently, polyoxometalates have been used in the sensitization of semiconductors[4] and sensitization of electrodes[5] and have been claimed to functionalize alkanes photochemically.[3c,6]

Polyoxometalates participate in catalytic processes as "oxygen relays" and/or as electron relays. The first case, in broad terms, represents, primarily, heterogeneous reactions. For instance, it has been shown that the oxidation of CO to CO_2 involves oxygen from the polyoxometalate which is, subsequently, replenished by atmospheric oxygen.[2] In homogeneous catalytic processes, in-cluding photocatalysis, polyoxometalates serve, primarily, as electron relays in electron-transfer and/or hydrogen-transfer reactions.

Key to their acting as homogeneous redox catalysts is the ability of polyoxometalates to accept and release a certain number of electrons without decomposition. An important step in the pho-tocatalytic cycle is the regeneration (reoxidation) of catalyst. Whereas, generally speaking, molybdates are better oxidizing reagents than tungstates, their reoxidation by dioxygen is very slow; many times, reoxidation requires the use of activated carbon with dioxygen or the use of hydrogen peroxide.[2] On the other hand, tungstates are difficult to reduce, yet their reoxidation by dioxygen is fast and effective.

Apart from generalities, such as reduced tungstates reoxidizing faster than molybdates and some rate constants being obtained with laser flash photolysis techniques,[7,8c] no systematic study for the reoxidation of polyoxometalates by dioxygen has been reported. Studies of the reoxidation of mixed molybdovanadates by dioxygen by Matveev et al. present an overall complicated picture that is rather different from the reoxidation of simple polyoxometalates discussed in this paper.[2b]

(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(2) (a) Misono, M. *Catal. Rev.—Sci. Eng.* **1987**, *29*, 269. (b) Kozhevnikov, I. V.; Matveev, K. I. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 11. (c) Kozhenvikov, I. V. *Russ. Chem. Rev. (Engl. Transl.)* **1987**, *56*, 811.
(3) (a) Hiskia, A.; Papaconstantinou, E. *Polyhedron* **1988**, *7*, 477. (b) Dimotikali, D.; Papaconstantinou, E. *Inorg. Chim. Acta* **1984**, *87*, 177. (c) Renneke, R. F.; Hill, C. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1526.
(4) Kiwi, J.; Gratzel, M. *J. Phys. Chem.* **1987**, *91*, 6673.
(5) Keita, B.; Nadjo, L. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *243*, 87.
(6) (a) Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528. (b) Muradov, M. Z.; Rustamov, M. I. *Dokl. Chem. (Engl. Transl.)* **1988**, *303*, 1051. (c) Zakrzewski, J.; Chauveau, F.; Giannotti, C. *Abstracts*, Joint Meeting of the Italian and French Photochemistry Groups, La Baume-les-Aix, France, Oct 1989; p 36.

(7) Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12.
(8) (a) Saidkhanov, S. S.; Kokorin, A. I.; Savinov, E. N.; Vokov, A. I.; Parmon, V. N. *J. Mol. Catal.* **1983**, *31*, 365. (b) Ioannidis, A.; Papa-constantinou, E. *Inorg. Chem.* **1985**, *24*, 349. (c) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 395. (d) Yamase, T. *Inorg. Chim. Acta* **1982**, *64*, L155. (e) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148. (f) Fox, M. A.; Cordona, R.; Gailard, E. *Ibid.* **1987**, *109*, 6347.

Light renders tungstate excited states effective oxidants for a variety of organic compounds and, due to their fast reoxidation (regeneration) by dioxygen, effective photocatalysts.[9]

This paper studies the mechanism of reoxidation by dioxygen of a series of polyoxotungstates, and to a limited extent 18-molybdodiphosphate. The effects of various parameters, such as hydrogen ion concentration, temperature, and degree of reduction, have been examined in order to find ways to optimize the photocatalytic cycle. Limited work has also been done with hydrogen peroxide, and the results are compared with those for dioxygen.

Experimental Section

Polyoxometalates were prepared according to well-established methods.[10] Photolysis was performed with a high-pressure Hg arc or a 150-W Xe lamp using a Pyrex filter. In cases where large quantities of reduced polyoxometalates were needed, a low-pressure Hg immersion lamp was used. Deaeration was performed with Ar scrubbed with V^{2+}. Kinetic studies were performed as follows: A deaerated solution of polyoxometalate, 5×10^{-4} M, in presence of, e.g., propan-2-ol, 2 M, of a certain pH and ionic strength, was photolyzed to a concentration of one-electron-reduced blue product of 0.6×10^{-4} M. The degree of reduction was followed by the characteristic spectra of the reduced species.[10d] Another identical solution without the polyoxometalate was oxygenated at the same time. The two solutions were mixed, and the rate of reoxidation was monitored at ~ 700 nm, which is the characteristic absorption of the reduced species. For rates slower than ~ 1 min, a thermostated recording spectrophotometer was used; for faster reactions, an Applied Photophysics stopped-flow apparatus was used. At least 10-fold excess oxygen was used to guarantee pseudo-first-order kinetics.

For the Arrhenius plots, one-electron-reduced $P_2W_{18}^{7-}$ and SiW_{12}^{5-} were used; the ionic strength was adjusted to 0.5 M ($NaClO_4$) and the pH to 2 and 3, respectively, with $HClO_4$. Different pHs had to be used to obtain reasonable rates. For instance, $P_2W_{18}^{7-}$ reoxidizes extremely slowly at pH >3, whereas SiW_{12}^{5-} reacts too rapidly at pH 2 and demands a stopped-flow apparatus.

In other experiments, the rate of reoxidation of $P_2W_{18}^{7-}$ by dioxygen was followed by monitoring the concentration of dioxygen with an oxygen electrode. In this case, a 10-fold excess of $P_2W_{18}^{7-}$ relative to dioxygen was used to secure pseudo-first-order kinetics.
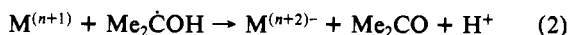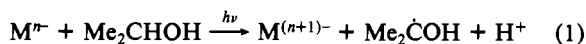
Kinetic studies with hydrogen peroxide were performed in a similar way. The concentration of hydrogen peroxide was established with the $KI-Na_2S_2O_3$ method.[11] Again, a 10-fold excess of hydrogen peroxide relative to reduced polyoxometalate was used for pseudo-first-order kinetics.

ESR spectra were run on a Bruker 2000D-SRC spectrophotometer equipped with a flat Suprasil cell. The one-electron-reduced polyoxometalates were obtained by photolysis as above. All ESR spectra were run with similar values of modulation, amplitude, gain, and MW power. ESR signals in the presence of dioxygen were obtained by mixing deaerated one-electron-reduced products with oxygenated solvent as above. In these cases, due to dilution, the gain was adjusted to match the intensity of the signal of the deaerated one-electron-reduced polyoxometalate.

Results and Discussion

It has been stated previously that a polyoxometalate, M^{n-}, photolyzed with UV and near-visible light, in the presence of an alcohol, e.g. Me_2CHOH, or other organic compounds, undergoes a series of photoreactions that result in stepwise reduction of the polyoxometalate and oxidation of the alcohol.[8]

The overall mechanism, for the first two reduction steps, may be presented as follows:

$$M^{n-} + Me_2CHOH \xrightarrow{h\nu} M^{(n+1)-} + Me_2\dot{C}OH + H^+ \quad (1)$$

$$M^{(n+1)} + Me_2\dot{C}OH \rightarrow M^{(n+2)-} + Me_2CO + H^+ \quad (2)$$

Generally, the photochemical reactions proceed until the redox potential of the reduced polyoxometalate, for instance, $M^{(n+2)-}$,

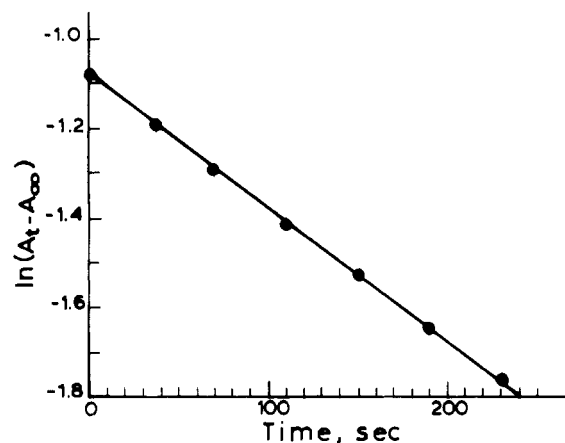(9) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1.
(10) (a) Pope, M. T.; Varga, G. M., Jr. *Inorg. Chem.* **1966**, *5*, 1249. (b) Pope, M. T.; Papaconstantinou, E. *Ibid.* **1967**, *6*, 1147. (c) Papaconstantinou, E.; Pope, M. T. *Ibid.* **1967**, *6*, 1152. (d) Varga, G. M., Jr.; Papaconstantinou, E.; Pope, M. T. *Ibid.* **1970**, *9*, 662.
(11) Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*, 3rd ed.; Wiley and Sons Inc.: New York, 1966; p 303.

Figure 1. Typical pseudo-first-order plot for the reoxidation of $P_2W_{18}^{7-}$ vs time ($[P_2W_{18}^{7-}] = 8 \times 10^{-5}$ M; $[O_2] = 8 \times 10^{-4}$ M; pH 1.7 ($HClO_4$); ionic strength to 0.5 M with $NaClO_4$).
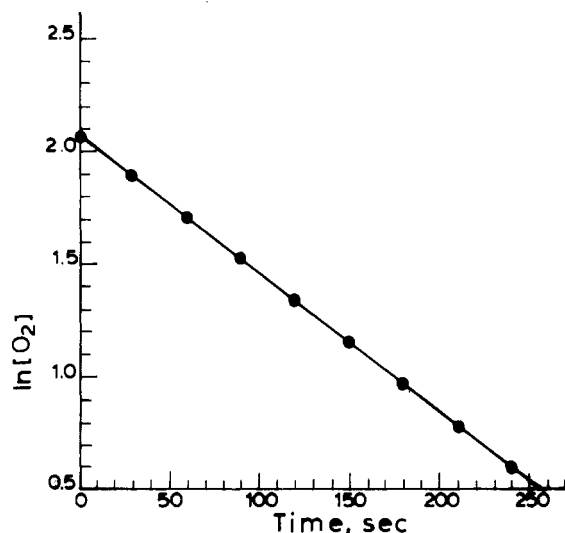
Figure 2. Pseudo-first-order rate plot for the consumption of dioxygen vs time ($[O_2] = 2.6 \times 10^{-4}$ M; $[P_2W_{18}^{7-}] = 2.9 \times 10^{-3}$ M; pH 1 ($HClO_4$); ionic strength to 0.5 M with $NaClO_4$).

is negative enough to reduce H^+ in the presence and absence of Pt catalyst (evolution of hydrogen)[8a-c].

$$M^{(n+2)-} + 2H^+ \rightarrow M^{n-} + H_2 \quad (3)$$
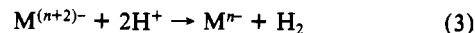
At this stage, a steady-state production of H_2 takes place with an overall quantum yield of 1%. The overall reaction is

$$Me_2CHOH \rightarrow Me_2CO + H_2 \quad (4)$$

In the presence of oxygen, a more effective oxidizing reagent than H^+, reoxidation of tungstates is fast and effective even for the one-electron-reduced species. Thus the photocatalytic cycle is obtained at the initial stage of photoreaction with quantum yields of $\sim 15\%$.[3a] In this case, reaction 3 is replaced, generally, by the reaction

$$M^{(n+1)-} + \frac{1}{4}O_2 + H^+ \rightarrow M^{n-} + \frac{1}{2}H_2O \quad (5)$$
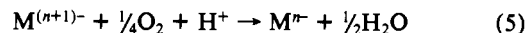
and the overall reaction becomes

$$Me_2CHOH + \frac{1}{2}O_2 \rightarrow Me_2CO + H_2O \quad (6)$$

The above is well established.[9]

Preliminary results with laser flash photolysis to generate the reduced tungstates, in solutions saturated with atmospheric O_2, showed that the reoxidation of a series of 12-tungstates, i.e., $PW_{12}O_{40}^{3-}$ (PW_{12}^{3-}), $SiW_{12}O_{40}^{4-}$ (SiW_{12}^{4-}), $FeW_{12}O_{40}^{5-}$ (FeW_{12}^{5-}), and $H_2W_{12}O_{40}^{6-}$ ($H_2W_{12}^{6-}$) reduced by one-electron, that is, PW_{12}^{4-}, SiW_{12}^{5-}, FeW_{12}^{6-}, and $H_2W_{12}^{7-}$, is 2-5 orders of magnitude faster than reoxidation by H^+.[7,8c]
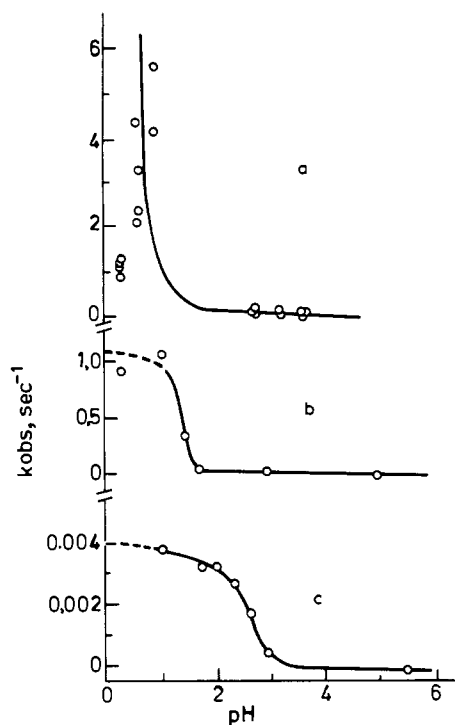
Figure 3. Variation of rate constants of reoxidation of the one-electron-reduced tungstates by dioxygen with the pH of the solution (pH adjusted with $HClO_4$; ionic strength to 0.5 M with $NaClO_4$): (a) $H_2W_{12}^{7-}$; (b) SiW_{12}^{5-}; (c) $P_2W_{18}^{7-}$.

Table I. Variation of Rate Constants of Reoxidation of Various One-Electron-Reduced Tungstates by Dioxygen with pH[a]

		k_{obs}, s^{-1} ($k_{obs}/[O_2]$, M^{-1} s^{-1})		
anion	$E_{1/2}$, V^b	low pH	intermediate pH, inflection point	high pH
$P_2W_{18}^{7-}$	0.34^c	3.8×10^{-3} (4.8)	2.0×10^{-3} (2.5)	0.0
SiW_{12}^{5-}	0.05^c	1.0 (1300)	0.5 (600)	2.7×10^{-2} (34)
$H_2W_{12}^{7-}$	-0.34^d	>5.5 (>6900)	3.0 (3800)	0.15 (190)

[a] Ionic strength to 0.5 M ($NaClO_4$); pH adjusted with $HClO_4$; $T \simeq 20$ °C. [b] Reduction potentials vs NHE.[10] [c] Values independent of pH; $E_{1/2} \simeq E°$.[10] [d] This value is pH-dependent below pH 4.9.[10]

Investigation of reaction 5 has shown the following:

a. The rate is first order with respect to polyoxometalate and first order with respect to dioxygen (Figure 1 and 2).

b. The rate is a function of pH (Figure 3). It can be seen that, at least for $P_2W_{12}^{7-}$, the rate becomes independent of [H$^+$] at low and high pH and is pH dependent at the inflection point. Experiments in that pH range with $P_2W_{18}^{7-}$ have shown the order with respect to H$^+$ to be 1.1 ± 0.4. Table I shows the characteristic rate constants at various pHs for comparison. It should be noted that, unlike other polyoxometalates that undergo hydrolytic degradation with increasing pH, the ones used in this study are known to be stable in the pH range of the experiments.[10]

c. Figure 4 shows Arrhenius plots for the reoxidation of the one-electron-reduced species, i.e., $P_2W_{18}^{7-}$ and SiW_{12}^{5-}, at the different pHs necessary to obtain reasonable rates. A good straight line is observed, from which the Arrhenius energies are calculated to be 66.3 and 40.2 kJ mol^{-1}, respectively.

d. Reoxidation rates follow thermodynamics. The more negative the reduction potential of the polyoxometalate, the faster is the reoxidation; see Table I and Figure 3.

e. The rate of reoxidation is also a function of the degree of reduction, which, again, follows thermodynamics as above. The higher the degree of reduction, the more negative the reduction potential and the faster the rate of reoxidation by dioxygen. This seems to contrast with recent results for 12-tungstophosphate in acetonitrile.[8f] Table II shows the reoxidation rate constants and the corrsponding redox potentials for various degrees of reduction of the 18-tungstodiphosphate and 18-molybdodiphosphate.
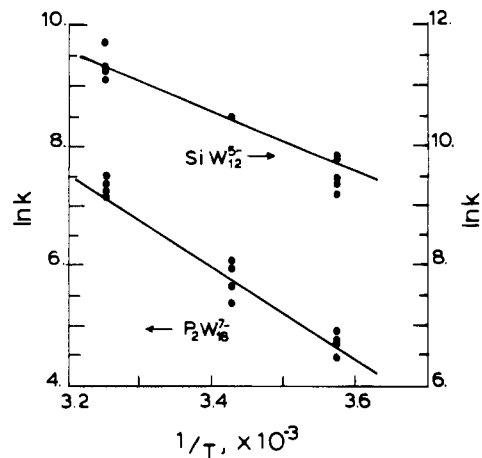

Figure 4. Arrhenius plots for reoxidation of SiW_{12}^{5-} and $P_2W_{18}^{7-}$ by dioxygen. In the calculation of the rate constant, $k = k_{obs}/[H^+][O_2]$, the variation of solubility of dioxygen with temperature was considered[20] (pH 3 and 2 ($HClO_4$), respectively; ionic strength to 0.5 M with $NaClO_4$; see text).

Table II. Rate Constants of Reoxidation of Reduced Polyoxometalates, at Various Degrees of Reduction, by Dioxygen[a]

redox step	$E_{1/2}$, V^b	k, M^{-1} s^{-1}	pH
$P_2W_{18}^{7-/6-}$	0.34^c	1.3	3
$P_2W_{18}^{8-/7-}$	0.14^c	6.9	3
$P_2Mo_{18}^{8-/6-}$	0.66^d	0.0	1
$P_2Mo_{18}^{10-/8-}$	0.34^d	0.0018	1

[a] Ionic strength to 0.5 M ($NaClO_4$); $T \simeq 20$ °C. [b] Reduction potentials vs NHE.[10] [c] Values independent of pH; $E_{1/2} \simeq E°$.[10] [d] pH-dependent values.

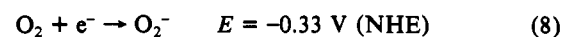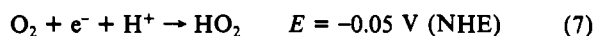**Table III.** Comparison of Rates of Reoxidation by Dioxygen and H_2O_2 of the 18-Tungstate and 18-Molybdate[a]

		rate const, M^{-1} s^{-1}	
redox step	$E_{1/2}$, V^b	O_2 oxidant	H_2O_2 oxidant
$P_2W_{18}^{7-/6-}$	0.34^c	4.8	0.2
$P_2Mo_{18}^{8-/6-}$	0.66^d	0.0	0.083

[a] pH = 1 ($HClO_4$); ionic strength to 0.5 M ($NaClO_4$); $T \simeq 20$ °C. [b] Reduction potentials vs NHE.[10] [c] Independent of pH; $E_{1/2} \simeq E°$. [d] pH-dependent.

f. Reoxidation of polyoxometalates was also studied, to a limited extent, with hydrogen peroxide. It turns out that reoxidation of $P_2W_{18}^{7-}$ by H_2O_2 is more than 1 order of magnitude slower than that by dioxygen (Table III). On the contrary, $P_2Mo_{18}^{8-}$ is not reoxidized by dioxygen, for all practical purposes, as has been mentioned, but it is reoxidized quite effectively by H_2O_2 (Table III).

Reduction of polyoxometalates by chemical and/or electrochemical means, in homogeneous media, is known to be an electron-transfer (ET) process in which polyoxometalates remain intact.[10] Consequently, reoxidation by dioxygen ought to be an ET reaction.

We present as follows the various reactions in which dioxygen participates as an oxidizing reagent, with the corresponding redox potentials:[12]

$$O_2 + e^- + H^+ \rightarrow HO_2 \qquad E = -0.05 \text{ V (NHE)} \qquad (7)$$

$$O_2 + e^- \rightarrow O_2^- \qquad E = -0.33 \text{ V (NHE)} \qquad (8)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E = 0.695 \text{ V (NHE)} \qquad (9)$$

$$HO_2 + e^- + H^+ \rightarrow H_2O_2 \qquad E = 1.44 \text{ V (NHE)} \qquad (10)$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad E = 1.76 \text{ V (NHE)} \qquad (11)$$

(12) Sawyer, D. T.; Nanni, E. J., Jr. Redox Chemistry of Dioxygen Species and their Chemical Reactivity. In *Oxygen and Oxy-radicals in Chemistry and Biology*; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; see also references therein.
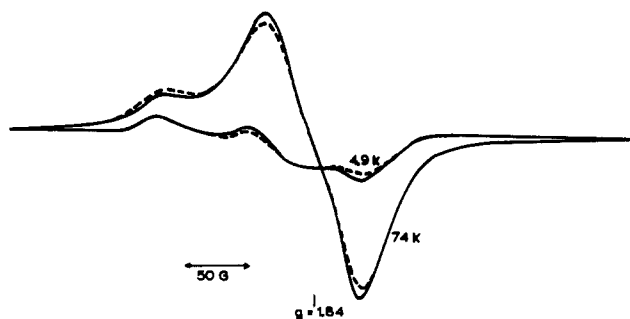
Figure 5. ESR signals of $P_2W_{18}^{7-}$, prepared by photolysis, in the absence (- - -) and presence (—) of dioxygen, at 74 and 4.9 K in 1×10^{-3} M $HClO_4$ and 2 M propan-2-ol (ionic strength to 0.5 M with $NaClO_4$; $[O_2]$ = 6×10^{-4} M; concentration of $P_2W_{18}^{7-}$ in the absence and presence of O_2 was 2.4×10^{-4} and 1.2×10^{-4} M, respectively; see text).

The one-electron-reduction potentials of the polyoxotungstates in question are summarized in Table I. It should be noted that (a) reduction of $P_2W_{18}^{6-}$ and SiW_{12}^{4-} is not accompanied by protonation over the pH range studied, whereas $H_2W_{12}^{6-}$ reduction is pH-dependent below pH 4.9 and (b) the one-electron-reduced products do not disproportionate.[10]
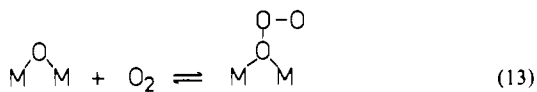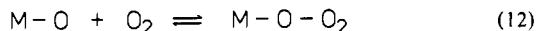
It can be seen that dioxygen is a rather poor one-electron oxidant, able to oxidize $H_2W_{12}^{7-}$ from the thermodynamic point of view, and partially SiW_{12}^{5-}, but not $P_2W_{18}^{7-}$. Nevertheless, any peroxy products produced would be very effective oxidants (reactions 10 and 11); see below.

The pH dependence cannot be attributed to any acid–base properties of the reacting species, since neither the polyoxometalates, with the exception of metatungstate as mentioned earlier, nor, of course, dioxygen is protonated or deprotonated in this pH range (Figure 3). Therefore, the pH dependence observed must be attributed to different causes.

A case to consider is the formation of an adduct between the one-electron-reduced tungstate and dioxygen. They both contain single electrons, so it is reasonable to assume an association resulting in pairing of the electrons.

There is a vast literature concerning dioxygen adducts with a variety of metal complexes,[13] in which dioxygen is coordinated to a free metal site. However, no free metal site is available in polyoxometalates. Tungsten ions are located in the center of an octahedral structure surrounded by six oxygens. Therefore, any association of dioxygen with polyoxometalates will have to occur through an oxygen, forming an ozonide type adduct, or a 7-coordinate peroxo moiety.[14] Another aspect to consider is the great number of peroxy compounds reported for molybdenum and tungsten, for instance $M(O_2)^{2-}$.[15]

Following the suggestion of a reviewer, we can consider the following possibilities for the polyoxometalate dioxygen adduct:

$$M-O + O_2 \;\rightleftharpoons\; M-O-O_2 \qquad (12)$$

$$(13)$$

$$(14)$$

Figure 6. ESR signals of SiW_{12}^{5-}, prepared by photolysis, in the absence (- - -) and presence (—) of dioxygen, at 74, 4.2, and 9.0 K in 1×10^{-3} M $HClO_4$ and 2 M propan-2-ol (ionic strength to 0.5 M with $NaClO_4$; $[O_2]$ = 0.8×10^{-4} M; concentration of SiW_{12}^{5-} was 1×10^{-3} M; see text).

where the first species on the left represent metal–oxygen bonds in the singly reduced polyoxoanions. According to Pope, the added electron occupies by b_2 (d_{xy}) orbital.[16] Coupling of this electron with the unpaired electrons of dioxygen would suggest that a 7-coordinate moiety (eq 14) is most likely,[14] as was kindly pointed out by a reviewer. In this case, the inflection point would correspond to the pK_a of the adduct.

Identical ESR signals were observed in experiments with $P_2W_{18}^{7-}$ (mixed a and b forms) at approximately liquid-nitrogen and liquid-helium temperatures and with SiW_{12}^{5-} at three different very low temperatures, in the presence and absence of oxygen, under very slow reoxidation conditions so that there would be no change in the signal due to reoxidation (Figures 5 and 6). Despite the fact that oxygen, being a triplet, exhibits a weak and complicated signal, there is nothing in these signals to suggest an association of tungstate with dioxygen. One, though, may always consider the possibility of minor interaction undetected by ESR spectroscopy; see below. However, Pope and Katsoulis have strong ESR evidence for complexation of dioxygen with $[MW_{11}Mn^{II}O_{39}]^{6-}$ (M = Si, Ge) at the manganese site, which is reversed by passage of nitrogen.[17] One may point out, unrelated to the purpose of this work, the different behavior of the ESR signals of the two polyoxometalates with temperature.

The overall picture is rather reminiscent of the behavior of various Cu^+ complexes oxidized to Cu^{2+} by dioxygen.[18] There is ample evidence from kinetic data that a Cu^+–dioxygen adduct, CuO_2^+, is formed that subsequently dissociates in the presence and absence of H^+ to form Cu^{2+} and peroxy products. No spectroscopic identificaton of the intermediate has been obtained except in a few cases.[19]

Designating the one-electron-reduced polyoxometalate, for simplicity, as M^-, we present the reaction mechanism, mainly for 18-tungstodiphosphate, as follows:

$$M^- + O_2 \rightarrow MO_2^- \qquad (15)$$

$$MO_2^- \rightarrow M + O_2^- \qquad (16)$$

$$(M^- + O_2^- \xrightarrow[\text{fast}]{2H^+} M + H_2O_2)$$

$$MO_2^- + H^+ \rightarrow M + HO_2 \qquad (17)$$

$$(M^- + HO_2 \xrightarrow[\text{fast}]{H^+} M + H_2O_2)$$

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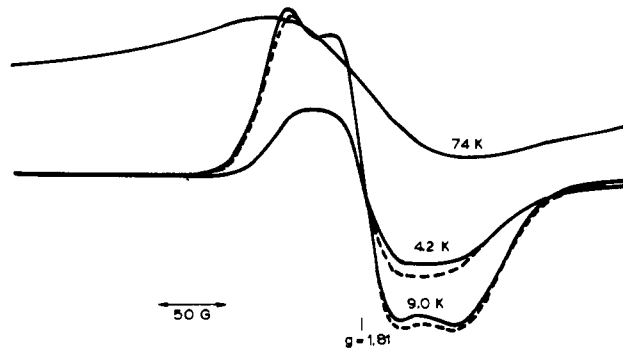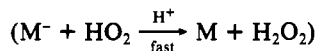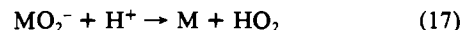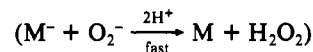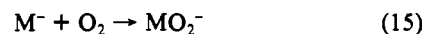
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Applying the steady-state approximation for MO_2^-, with reactions 16 and 17 the rate-determining steps, we obtain

$$\frac{d[M^-]}{dt} = \frac{k_{16} + k_{17}[H^+]}{k_{-15} + k_{16} + k_{17}[H^+]} k_{15}[M^-][O_2]$$

At low pH, $k_{17}[H^+] \gg k_{16} + k_{-15}$ and rate = $k_{15}[M^-][O_2]$, independent of H^+ concentration.

At high pH, $k_{16} \gg k_{17}[H^+]$; therefore, rate = $(k_{16}/(k_{-15} + k_{16}))k_{15}[M^-][O_2]$, again independent of H^+ concentration.

In intermediate cases, the reaction depends on H^+ concentration. As mentioned earlier, experiments at the inflection point have shown the order, with respect to H^+, to be 1.1 ± 0.4 for the 18-tungstodiphoshate.

Thus, the inflection point, as in the case of reoxidation by dioxygen of many Cu^+ complexes, is attributed to a kinetic phenomenon and does not reflect the pK_a of the dioxygen adducts.

Limited work with H_2O_2 has shown that it behaves differently. As mentioned earlier, hydrogen peroxide is less effective with tungstates but more effective with molybdates (Table III).

A different kind of mechanism ought to operate here. Similar behavior seems to have been observed with Cu^+ complexes.[19] H_2O_2 is effective oxidant even for complexes with high redox potential (reaction 11). It has been found that Cu^+ complexes with low potential react rapidly with dioxygen to form preferentially H_2O_2, whereas the slowly reacting ones, i.e., those with high potential, give complete reduction to water.[19]

Experiments with one-electron-reduced 18-tungstodiphosphate have shown that the rate of reoxidation by dioxygen monitored by following the consumption of $P_2W_{18}^{7-}$ is 2 times faster than the rate determined when the consumption of dioxygen was followed, suggesting that dioxygen participates as a two-electron
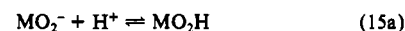
oxidant and that H_2O_2 ought to be the product. This is also enhanced by the considerably slower reaction of hydrogen peroxide relative to dioxygen with $P_2W_{18}^{7-}$ (Table III).

However, no hydrogen peroxide could be detected with the experimental method used, which, nevertheless, could only detect concentrations higher than those anticipated here. Similarly, in many cases with Cu^+ complexes, in which hydrogen peroxide has been claimed to be the product, the latter could not be detected.[19,21]

Registry No. $P_2W_{18}O_{62}^{6-}$, 90751-95-4; $SiW_{12}O_{40}^{4-}$, 12363-31-4; $H_2W_{12}O_{40}^{6-}$, 12207-61-3; $P_2Mo_{18}O_{62}^{10-}$, 137626-08-5; $P_2Mo_{18}O_{62}^{8-}$, 92844-04-7; $P_2W_{18}O_{62}^{7-}$, 12504-08-4; $P_2W_{18}O_{62}^{8-}$, 117404-39-4; $P_2Mo_{18}O_{62}^{6-}$, 57609-49-1; O_2, 7782-44-7; H^+, 12408-02-5; H_2O_2, 7722-84-1.

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(21) One may also consider a slightly modified mechanism that involves an acid–base equilibrium, reaction 15a, and dissociation of the MO_2H adduct, reaction 18, rather than attack by H^+ on MO_2, reaction 17. In this case, the pK_as of the dioxygen adducts ought to be involved:

$$M^- + O_2 \rightleftharpoons MO_2^- \tag{15}$$

$$MO_2^- + H^+ \rightleftharpoons MO_2H \tag{15a}$$

$$MO_2^- \rightarrow M + O_2^- \tag{16}$$

$$MO_2H \rightarrow M + HO_2 \tag{18}$$

We will defer discussion on this mechanism, until more data are available to support or refute it.

Contribution from the Department of Chemistry,
Baylor University, Waco, Texas 76798

Mechanistic Studies of the Oxidative Cleavage of the Molybdenum–Mercury Bonds in [CpMo(CO)₂(PPh₃)]₂Hg

Chen C. Lin and Stephen L. Gipson*

Chemical or electrochemical oxidation of the trimetallic complex [CpMo(CO)₂(PPh₃)]₂Hg (Cp = η⁵-C₅H₅) occurs in two one-electron steps. The first electron transfer generates a transient cation which undergoes Mo–Hg bond cleavage to generate a 16-electron species, [CpMo(CO)₂(PPh₃)]⁺, and a mercury-centered radical, CpMo(CO)₂(PPh₃)Hg•. To account for the products, it is proposed that the radical dimerizes and then reacts with half of the available 16-electron cation to form an observable pentametallic intermediate. The second electron transfer generates [CpMo(CO)₂(PPh₃)Hg]⁺ and returns the 0.5 mol of [CpMo(CO)₂(PPh₃)]⁺ which was incorporated into the intermediate. The mercury-containing cation subsequently eliminates metallic mercury to yield a second mole of [CpMo(CO)₂(PPh₃)]⁺. The 16-electron cation coordinates solvent or other available neutral or anionic ligands to yield 18-electron complexes.

Introduction

There has long been widespread interest in the reductive and oxidative cleavages of metal–metal bonds in transition-metal organometallic compounds.[1–14] For binuclear species, these

cleavages are often two-electron processes producing synthetically useful anionic or cationic fragments. Cationic fragments resulting from oxidations are generally coordinatively unsaturated and so

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