*Inorg. Chem.* **1993,** *32,* 5797–5799 **5797**

# Correlation between One-Electron Reduction and Oxygen–Oxygen Bond Strength in $d^0$ Transition Metal Peroxo Complexes

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*Received July 20, 1993*[⊗]

In a series of V(V), Cr(VI), Mo(VI), and W(VI) peroxometal complexes containing different ligands, a correlation has been found between their oxygen–oxygen bond strengths, measured by the corresponding vibrational frequencies, and their ability to act as one-electron acceptors, provided by the reduction potentials. The correlation holds for complexes of the same metal containing different ligands as well as for complexes of the various metals containing the same ligand. The nature of the ligands in affecting the one-electron-oxidizing ability of the peroxo complexes appears to play a more important role than the nature of the metal. The correlations found indicate that the electron transfer occurs at less negative potentials for those peroxo complexes where the oxygen–oxygen bond is shorter.

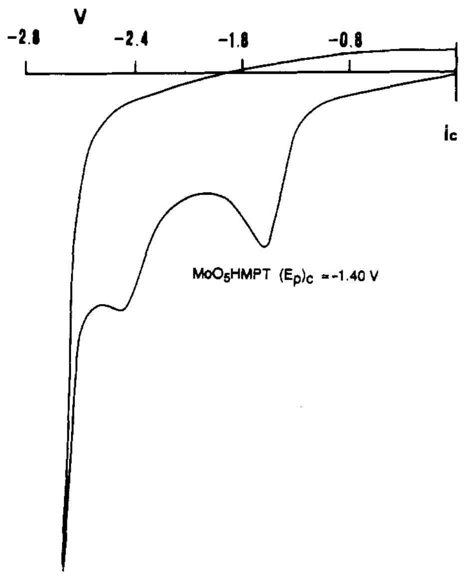

**Figure 1.** Cyclic voltammetry of $MoO_5(HMPT)$ ($1 \times 10^{-3}$ mol $L^{-1}$) in DMF (supporting electrolyte TBAP (0.1 mol $L^{-}$), working electrode glassy carbon, reference electrode SCE; scan rate 100 mV $s^{-1}$.

Among the various oxidants of organic substrates, $d^0$ transition metal peroxo complexes, namely Ti(IV), V(V), Cr(VI), Mo(VI), and W(VI) derivatives, attract continuously growing interest because of their versatility and selectivity.[1] Examples of these features include the stereospecific olefin epoxidation by Mo(VI)–oxo–diperoxo complexes,[2] the chemoselective oxidation of thioethers to sulfoxides by V(V)–oxo–monoperoxo compounds,[3] and the almost enantiospecific oxidation of allylic alcohols[4] and thioethers[5] by Ti(IV)–alkylperoxo derivatives. Such reactions belong to the family of heterolytic electrophilic oxidations.[6] Thus, the delivery of a peroxide oxygen to the nucleophilic substrate amounts to an $S_N2$ displacement by the substrate on the oxygen–oxygen bond of the peroxometal complex.[6a] More recently, radical oxidations involving Mo(VI)- and V(V)–peroxo derivatives also received increasing attention in view of their synthetic scope. Thus, V(V)–picolinato peroxo complexes have been shown to hydroxylate benzene[7] and substituted benzenes[8] to the corresponding monophenols under very mild conditions. Furthermore, Mo(VI)–picolinato and –picolinate *N*-oxido peroxo complexes oxidize primary alcohols to aldehydes,[9] without any overoxidation to carboxylic acids, and diols to $\alpha$-diketones[10] in a process which involves the intermediacy of ketyl radicals.[10] Such mechanistic shifts from heterolytic to homolytic reactivity for the same metal ion are clearly determined by the nature of coordination sphere of the metal. Accordingly, the oxidative behavior of these oxidants could be properly tuned by a careful choice of the ligands. To this aim, a valuable step forward would be the availability of a correlation between some physical property of the peroxo complex and the nature of its coordination sphere. Such a correlation is not, as yet, available. For example, a few years ago Vaska[11] examined several peroxometal complexes, including $d^0$ derivatives, reaching the conclusion that there was no relationship whatsoever between the O–O distances, as measured in the crystal structure,

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1993.

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(12) The IR spectra were recorded on a FT-IR Perkin-Elmer 1600 instrument by employing KBr pellets.

0020-1669/93/1332-5797$04.00/0

**Table I.** Stretching Frequencies (M=O and O—O) and Reduction Peak Potentials for a Series of $d^0$ Peroxometal Complexes Containing Various Ligands

| complex[a] | abbrev | $\nu$(M=O), $cm^{-1}$ | $\nu$(O—O), $cm^{-1}$ | $E_p$(cat), V |
|---|---|---|---|---|
| $VO(O_2)(C_5H_4NCO_2)(H_2O)_2$ | $VO_3$(Pic) | 980.1 | 938.0 | −1.26 |
| $VO(O_2)(C_5H_4NOCO_2)(H_2O)_4$ | $VO_3$(Pico) | 957.9 | 909.8 | −1.26 |
| $[CrO(O_2)_2(C_5H_4NCO_2)]^-H^+$ [b] | $CrO_5$(Pic) | 950.1 | 934.6 | −1.22 |
| $MoO(O_2)_2(OP(NMe_2)_3)$ | $MoO_5$(HMPT) | 965.6 | 875.5 | −1.44 |
| $[MoO(O_2)_2(C_5H_4NCO_2)]^-Bu_4N^+$ | $MoO_5$(Pic) | 947.1 | 860.0 | −1.78 |
| $[MoO(O_2)_2(C_5H_4NOCO_2)]^-Bu_4N^+$ | $MoO_5$(Pico) | 944.9 | 864.2 | −1.54 |
| $[MoO(O_2)_2(C_6H_5CO_2)]^-Bu_4N^+$ | $MoO_5$(Benz) | 973.5 | 868.2 | −1.56 |
| $WO(O_2)_2(OP(NMe_2)_3)$ | $WO_5$(HMPT) | 972.2 | 885.3 | −1.30 |
| $[WO(O_2)_2(C_5H_4NCO_2)]^-Bu_4N^+$ | $WO_5$(Pic) | 952.6 | 879.0 | −1.66 |
| $[WO(O_2)_2(C_5H_4NOCO_2)]^-Bu_4N^+$ | $WO_5$(Pico) | 953.0 | 883.1 | −1.44 |

[a] The synthesis of the peroxo complexes has been already reported; see refs 2, 7, 9, and 15. [b] This novel chromium oxo–diperoxo complex was synthesized by adding to a strongly acidic ($H_2SO_4$) aqueous solution of $Cr_2O_7^{2-}$ (1.7 mmol in 50 mL) 1 mL of $H_2O_2$ (35% w/v). The peroxo species thus formed was extracted into 50 mL of ether, and the extract was dried over $MgSO_4$. Subsequently, 1 equiv of picolinic acid was added, causing the precipitation of the peroxo complex (peroxidic titer ≥98%) as a blue solid, stable for weeks at 4 °C in the dark. IR and $^1$H-NMR analyses of the material are in agreement with the formula indicated.

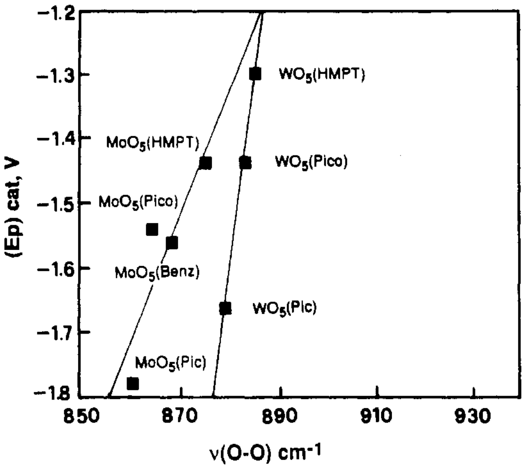

**Figure 2.** Plot of observed reduction potentials as a function of O–O stretching frequencies for Mo(VI) and W(VI) peroxo complexes containing different ligands. (Correlation for Mo(VI) species **r** = 0.93; correlation for W(VI) species **r** = 0.99.)

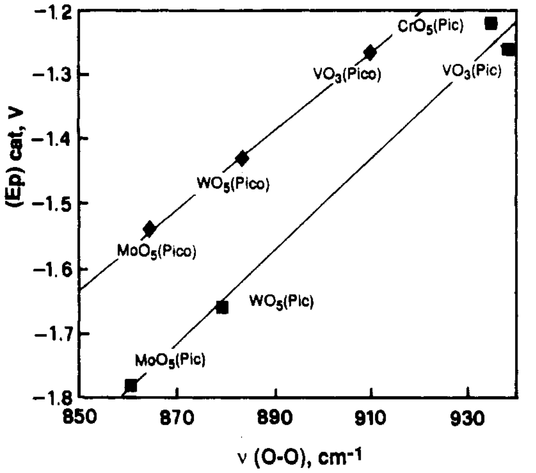

**Figure 3.** Plot of observed reduction potentials as a function of O–O stretching frequencies for a series of peroxometal complexes containing either Pic or Pico ligands. (Correlation for species containing the Pic ligand **r** = 0.99; correlation for species containing the Pico ligand **r** = 0.99.)

and the chemistry of the peroxo species. Despite such a disappointing precedent, we were attracted by the possibility that the various ligands could be directly responsible of some changes in the physical properties of the peroxide group and that, in turn, such changes could be related to the reactivity of the peroxo complexes. The physical property selected was the O–O vibrational frequency, which can be measured by FT-IR techniques with high accuracy.[12] In addition, it is available also for noncrystalline materials. As a reactivity probe, the search was for a process as simple as possible. Also in the light of the recognized relevance of the radical oxidations for $d^0$ peroxometal complexes, an appropriate feature should be their ability to act as one-electron acceptors. Such an ability may be measured by their reduction peak potentials, $E_p$(cat)[13] (see as an example Figure 1). Table I lists all the pertinent information obtained in our investigation, whereas Figures 1 and 2 show the correlations obtained when the O–O stretching frequencies for the same metal ion, namely Mo(VI) or W(VI), with different ligands are plotted against the reduction potentials (Figure 2) and when the same plot is made with different metal ions containing the same ligand, Pic (picolinato anion) or Pico (picolinate *N*-oxido anion) (Figure 3). As can be seen, all the correlations give satisfactory straight lines, thus suggesting that indeed the O–O bond strength and the capability to accommodate an electron are closely related features determined by the nature of both the metal and the ligands. The observation that the slopes of the straight lines of Figure 3, where different metals with the same ligand are correlated, are smaller than those of Figure 2, referring to the same metal with different ligands, leads to the finding that the role played by the ligands in determining the general behavior of $d^0$ peroxo complexes is more important than that played by the metal itself. On the other hand, this agrees with the experimental observation that derivatives of the same metal exhibit different oxidation chemistries depending on their coordination spheres. Further significant information provided by the inspection of Figures 2 and 3 is that the reduction potentials of the various species shift to less negative values with increasing strength of the O–O bond. The latter, in turn, is larger for complexes containing neutral ligands, such as HMPT (hexamethylphosphoric triamide), than for those containing anionic molecules, such as Pic and Pico.

Thus, the reduction potentials of vanadium and chromium derivatives, which show very strong O–O bonds, are almost the same, in agreement with the common notion that radical reactions are more likely for these two metal peroxo complexes than for those of Mo(VI) and W(VI).[14] Finally, some hints on the electrode

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(13) All the electrochemical measurements were carried out in the same solvent, *i.e.* DMF, thus avoiding problems related to liquid-junction potentials. Owing to the large irreversibility of the electrode process, cyclic voltammetry, which gives directly the *E*p values, is the technique of choice. Cyclic voltammetry measurements were run with an EG&G-PAR 273 potentiostat/galvanostat controlled by an EG&G-PAR universal programmer. A Hewlett Packard X-Y 7090 A plotter was used to record the current voltage output for 100 mV/s sweep rate. A conventional three-electrode system consisting of a glassy carbon working electrode (o.d. 3 mm), a platinum wire counter electrode, and a saturated calomel electrode (SCE) as reference was used. The solutions were usually 0.1 mol $L^{-1}$ in supporting electrolyte (TBAP) and $1 \times 10^{-3}$ mol $L^{-1}$ in peroxo complex. All the solutions were deoxygenated by bubbling a nitrogen stream for at least 10 min prior the recording of the voltammetric data. Controlled-potential electrolysis confirms the occurrence of one-electron reduction processes.

process can be offered. We find that the M═O vibrational frequencies, reported in Table I, do not correlate to any extent with the reduction potentials, at variance with the O–O vibrational frequencies. This might be taken as evidence that the peroxide group coordinated to the metal plays a role more important than that of the metal itself in the electron-transfer process. The chemistry subsequent to such a process, which likely contributes to the irreversibility of the electrode reaction, is as yet unknown, even though the cleavage of the O–O bond appears a likely reaction.

In summary, we have shown for the first time, to the best of our knowledge, that a physical property of $d^0$ peroxometal complexes, namely the IR O–O bond frequency, is related to their ability to act as one-electron acceptors in very simple electrode processes. The extension of our results to radical reactions involving such oxidants, even those triggered by SET from the substrate to the complex,[15] may be rather misleading, because of the complexity of these oxidative processes, which usually are chain radical reactions involving several steps.[8] Nevertheless our findings may be considered a useful tool for mechanistic studies in both organic chemistry and biochemistry.

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