

REVIEW COMMENTARY

THE VERSATILE CHEMISTRY OF PEROXO COMPLEXES OF VANADIUM, MOLYBDENUM AND TUNGSTEN AS OXIDANTS OF ORGANIC COMPOUNDS

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The oxidation of organic compounds by hydrogen peroxide, catalysed by transition metal derivatives, e.g. V(V), Mo(VI) and W(VI) complexes, involves the formation of peroxometal complexes. These are much more efficient oxidants than hydrogen peroxide so that the catalysed reactions are of remarkable synthetic significance. Several peroxometal complexes can be isolated and used as stoichiometric oxidants. An appealing feature of these oxidants is their versatility, as demonstrated by the fact that they are able to oxidize substrates such as alkenes, alcohols, ketones, sulphur, phosphorus and nitrogen derivatives and even aromatic and aliphatic hydrocarbons. Either polar or radical oxidations may take place. The reactivity depends on the nature of the metal and especially on the nature of the ligands coordinated to the metal. Therefore, an important goal consists in predicting the reactivity of peroxometal complexes on the basis of their structural features. Examples presented demonstrate that structure–reactivity correlations may be established. However, the effect of the ligands appears to be complex so that care must be exercised in drawing general conclusions.

Peroxidic compounds are widely used as stoichiometric oxidants of organic compounds.^{1,2} Peroxides which have found synthetic applications^{1,2} include alkyl hydroperoxides, organic peracids and dioxiranes, all, at least formally, derived from hydrogen peroxide, by substitution of one or both hydrogen atoms. Therefore, in all these molecules a relatively weak ($120\text{--}190\text{ kJ mol}^{-1}$)³ O—O bond is present. In the oxidative process this bond is cleaved. Two main modes of cleavage^{4,5} can be envisaged. If the bond is cleaved heterolytically, polar oxidations will take place, whereas if the cleavage is homolytic, radical oxidations will be observed. In polar reactions, if reactivity is the only parameter taken into account in order to establish the oxidation power, one may conclude that organic peracids⁶ and also dioxiranes⁷ are indeed very effective reagents. They oxidize a variety of organic compounds under relatively mild conditions and with selectivities ranging from fair to excellent.^{6,7} There are, however, other considerations

which would suggest employing hydrogen peroxide. Among these, perhaps the most convincing one, which applies in particular to large-scale preparations or to industrial processes, is related to the fact that hydrogen peroxide is by far the least environmentally demanding among the peroxides; in fact, water is the only by-product of these reactions.⁸ Unfortunately, hydrogen peroxide is a rather weak oxidant. Thus, in order to become synthetically significant, the oxidations by hydrogen peroxide need to be catalysed.⁹ This has stimulated a large-research effort aimed at finding effective catalysts. Among the oldest, but very efficient, catalysts which have been discovered, the derivatives of some transition metal ions, i.e. V, Mo and W, in their highest oxidation states, are still under active investigation.^{3,10} The general mechanism of the catalysis is well understood⁹ (Scheme 1).

The metal precursor adds hydrogen peroxide in an equilibrium process largely shifted to the right.¹¹ No redox chemistry is involved in this step. In fact, the metal derivatives are already in their highest oxidation states and, on the other hand, they are not able to act as

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The oxidation of the alcoholic function can be carried out even if other oxidizable groups, e.g. a double bond, are present in the molecule.¹⁸ The oxidation of primary alcohols becomes unselective under catalytic conditions in the presence of hydrogen peroxide¹⁹ owing to solvolysis of the ligand followed by formation of polynuclear molybdenum complexes.²⁰ These are less selective catalysts so that carboxylic acids are formed. By contrast, both alkene epoxidation by neutral peroxomolybdenum complexes (see 2 in Scheme 2)^{15,20} and hydroxylation of benzene and substituted benzenes by peroxovanadium complexes (see 4 in Scheme 2)^{17,21} proceed under catalytic conditions.^{20,21}

The examples in Scheme 2 show that peroxometal complexes are versatile oxidants capable of reacting with very different substrates. This also suggests that several mechanistic pathways are accessible to such oxidants.^{5,22,23} This conclusion is corroborated by the information provided in Scheme 3 in which some other selected processes are shown.

It is commonly accepted on the basis of several pieces of evidence that olefins epoxidation, and the oxidation of heteroatoms such as sulphur and nitrogen, are clean, polar reactions.^{9,22,23} The oxidation of cyclic ketones to lactones, an example of the Baeyer–Villiger reaction, is still ill-defined from a mechanistic point of view.^{24,25} The oxidation of alcohols and the hydroxylation of aromatic and aliphatic hydrocarbons are radical reactions.¹⁷ In particular, the formation of phenol from benzene, carried out by peroxovanadium complexes, is a complicated radical chain process.^{17b,c}

It would be very desirable to be able to predict the kind of reactivity of peroxometal complexes on the basis of some of their measurable properties. This is not yet possible because, as will be discussed later, the effect of the ligands on the oxidative behaviour of peroxometal complexes is a combination of several factors. Nevertheless, a step forward in the direction of predicting the reactivity has been made by establishing the correlation shown in Figure 1.²⁶

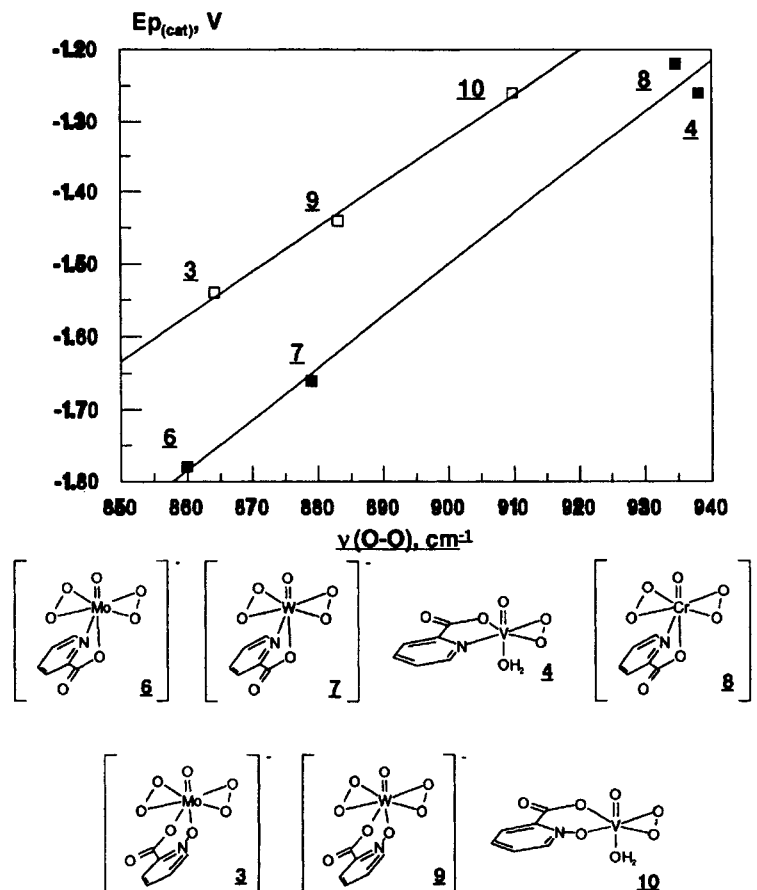


Figure 1. Plots of observed reduction peak potentials as a function of O—O stretching frequencies for a series of peroxo complexes containing either picolinic acid anion or picolinate *N*-oxido anion as ligands

In particular, the ability of peroxometal complexes to act as one-electron acceptors, as measured by their reduction peak potential, obtained by cyclic voltammetry,²⁷ has been correlated with the O—O stretching frequency, i.e. with the strength of the bond, measured by IR spectroscopy. Peroxo complexes of different metals containing the same ligand have been examined. It may be seen that the stronger the oxygen—oxygen bond, the easier is the electron transfer to the complex. Therefore, peroxo vanadium and chromium complexes, in which the O—O stretching frequency is the largest, are reduced at lower potentials than molybdenum and tungsten derivatives. This fits with the common notion that radical oxidations are more frequent when peroxo chromium and vanadium complexes are used.^{1,17} A correlation may also be established among peroxo complexes of the same metal containing different ligands.²⁶ This is shown in Figure 2, in which only molybdenum and tungsten derivatives are considered

because the number of stable peroxovanadium and chromium complexes is too small.

A comparison of the slopes of the straight lines of Figures 1 and 2 reveals a further interesting aspect. It appears that the nature of the ligands plays a more important role than the nature of the metal in determining the one electron acceptor ability of peroxo complexes. This again underlines the relevance of the coordination sphere of such oxidants in determining their behaviour. It would be hazardous however, to make predictions about the oxidative ability of peroxo complexes based only on their reduction peak potential. The case of peroxomolybdenum complexes is instructive in this respect. As it may be seen in Scheme 4, the reduction peak potential of the four peroxomolybdenum complexes examined appears to be directly related to the electron density on the metal.²⁸ Thus the anionic MoO₃PIC (6) and MoO₃PICO (3) complexes are reduced at more negative potentials than MoO₃DIPIC

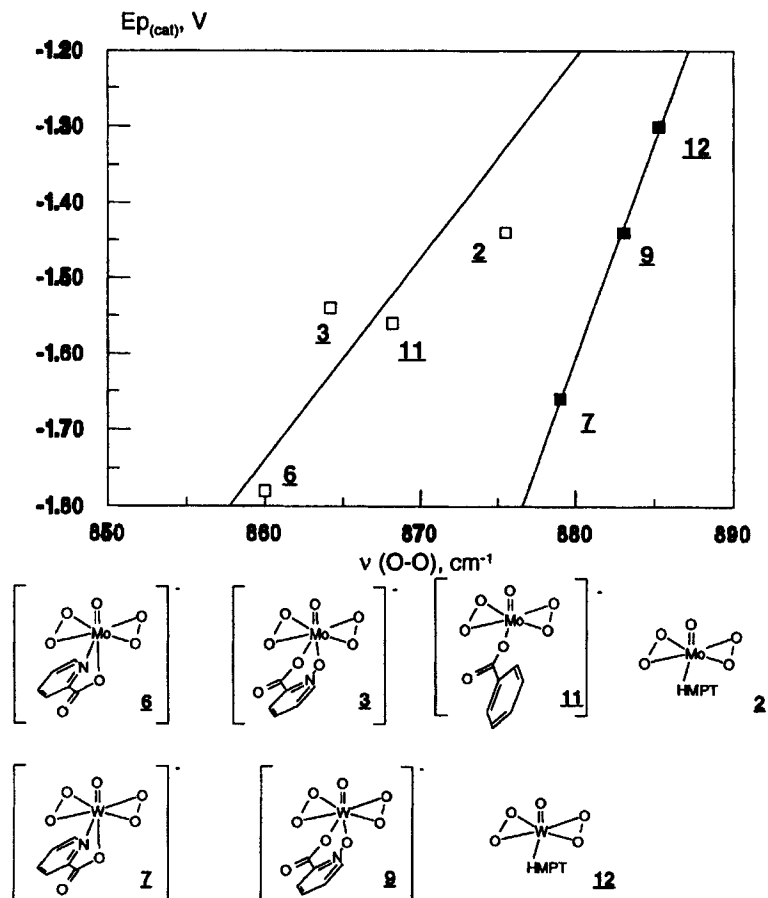
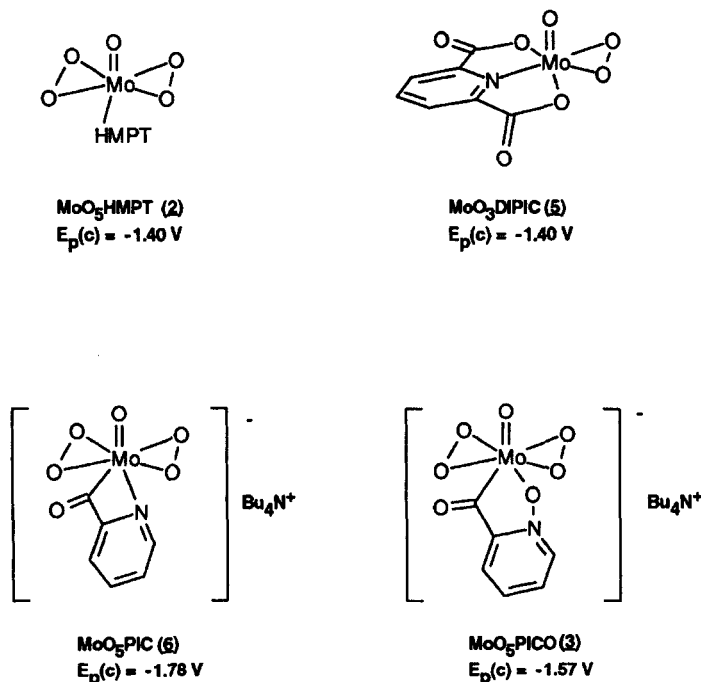


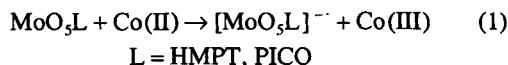
Figure 2. Plots of observed reduction peak potentials as a function of O—O stretching frequencies for Mo(VI) and W(VI) peroxo complexes containing different ligands



Scheme 4. Examples of isolated peroxomolybdenum complexes with corresponding reduction peak potentials

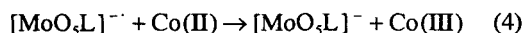
(5) and MoO₅HMPT (2) neutral species.²⁷ On this basis, one might predict that in the decomposition reaction induced by a one electron donor, e.g. Co(acac)₂ the neutral species should be more reactive than the anionic species. As indicated by the data in Table 1, the opposite behaviour is observed.²⁸

In fact, the presence of Co(II) induces the complete decomposition of MoO₅PICO in 8 h whereas in the same time interval only 30% of MoO₅HMPT is decomposed. The rationale of these findings is based on the fact that the decomposition is a radical chain reaction²⁸ in which the initiation is the oxidation of Co(II) to Co(III) by the peroxo complex;

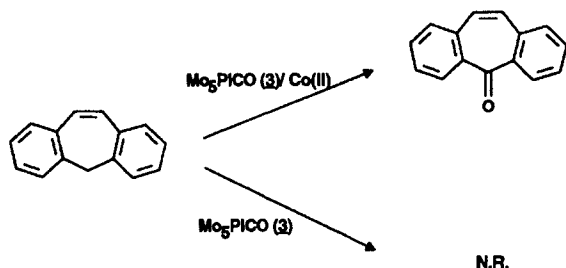
Table 1. Co(II)-catalysed decomposition of Mo(IV) peroxo complexes (0.012 mol l⁻¹) in DCE at 40 °C

Complex	Co(acac) ₂ , (mol l ⁻¹)	Time (h)	(%) Peroxide consumed
MoO ₅ DIPIC	0.0012	24	20
MoO ₅ HMPT	0.0012	24	80
MoO ₅ HMPT	0.00036	8	30
MoO ₅ PIC	0.00036	8	20
MoO ₅ PICO	0.00036	8	100

In order to establish the chain, the steps of equations (2) and (3) followed by the termination step of equation (4) must be considered:

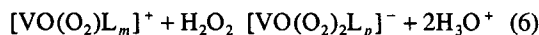
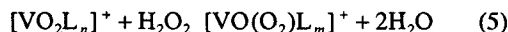


Based on the electrochemical data, MoO₅HMPT (2) should be more reactive than MoO₅PICO (3) in reaction (1) so that the initiation should be faster for the neutral than for the anionic complex. On the other hand, the termination step, equation (4) is probably much faster when the oxidant is [MoO₅HMPT]^{·-} than when it is [MoO₅PICO]^{·-}, which is formally a dianionic species. As a result, in spite of the fact that MoO₅HMPT is a better one electron acceptor than MoO₅PICO, the decomposition reaction of the former complex is slower than that of the latter because the termination of the chain reaction is more efficient when MoO₅HMPT is used. It may be mentioned, in passing, that the addition of Co(acac)₂ to a solution of MoO₅PICO in dichloroethane activates the peroxo complex towards the oxidation of alkenes and saturated hydrocarbons whereas in the absence of Co(II), MoO₅PICO is completely inert toward such substrates, (Scheme 5).²⁸ The formation of molybdenum radical species, characterized by a peculiar oxidizing ability, has been suggested.²⁸



Scheme 5. Co(II)-induced reactivity of MoO_3PICO in dichloroethane

In other systems, the electronic character of the ligands and the reactivity of the peroxo complexes may be correlated. This is the case of peroxovanadium complexes in aqueous solution.²⁹ This chemistry is receiving increasing attention as a consequence of the discovery that vanadium is almost ubiquitous in plants and living organisms, including the human, while little is known on its role in biochemical processes.^{30,31} The method of choice for studying the behaviour of peroxovanadium species in aqueous solution is ^{51}V NMR spectroscopy.³² This technique makes it relatively simple to identify the kind of peroxo complexes formed in solution by adding variable excesses of hydrogen peroxide to a vanadium(V) precursor, NH_4VO_3 , at various pH values, according to the following equilibria.³³



where L = water or organic ligands, e.g. picolinic and pyrazinic acid, pyridines and anilines.

The ^{51}V NMR chemical shifts can be well correlated with the electronic properties of the ligands, as shown in the Hammett plot in Figure 3 in the case of diperoxovanadium complexes containing variously substituted pyridines as ligands.²⁹ In particular, the increase of the electron-donating character of the ligands enhances the magnetic shielding of the metal so that the chemical shifts values become more negative.²⁹

A similar effect is observed in the case of monoper-

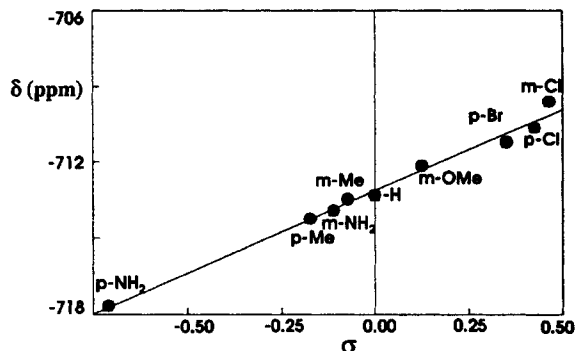


Figure 3. Hammett-type plot correlating the sigma values with ^{51}V NMR chemical shifts for a series of diperoxovanadium complexes containing variously substituted pyridines as ligands ($r = 0.995$, $\rho = 29.8 \pm 0.3$)

oxo complexes containing bidentate ligands, as indicated by the data in Table 2.²⁹ In this case, the reactivity of the peroxo complexes decreases when the negative charge on the metal, brought in by the ligands and measured by the ^{51}V NMR chemical shifts, is increased. In fact, it may be observed in Figure 4 that the ability to decompose selected monoperoxovanadium complexes decreases on decreasing the electron-donating properties of the different ligands.²⁹

In conclusion, the information so far available on the role of the ligands on the oxidative ability of peroxo complexes may be summarized as follows:

- (i) The nature of the ligands can dramatically change the reactivity of peroxo complexes, which may shift from polar to radical oxidants even when the metal is the same.
- (ii) In simple oxidations, either polar or radical, an increase in the electron-donating character of the ligands causes a decrease in the reactivity. Therefore, the possibility of estimating the amount of negative charge on the metal by electrochemical or spectroscopic methods is of great help in making reactivity predictions.
- (iii) The effect of the ligands, however, may be much

Table 2. ^{51}V NMR chemical shifts (δ) from VOCl_3 for monoperoxovanadium complexes containing different carboxypicolinic acids²⁸

Complex	δ (ppm)	Complex	δ (ppm)
VO_3PIC	-600.6	$[\text{VO}_3(\text{PIC})_2]^-$	-632.6
$\text{VO}_3\text{PIC}(3\text{-COOH})$	-595.1	$[\text{VO}_3(\text{PIC}(3\text{-COOH}))_2]^-$	-617.8
$\text{VO}_3\text{PIC}(4\text{-COOH})$	-596.3	$[\text{VO}_3(\text{PIC}(4\text{-COOH}))_2]^-$	-624.0
$\text{VO}_3\text{PIC}(5\text{-COOH})$	-595.9	$[\text{VO}_3(\text{PIC}(5\text{-COOH}))_2]^-$	-622.3
$\text{VO}_3\text{PIC}(6\text{-COOH})$	-597.5	$[\text{VO}_3(\text{PIC}(6\text{-COOH}))_2]^-$	— ^a

^a Formation of complex $[\text{VO}_3(\text{PIC}(6\text{-COOH}))_2]^-$ was not detected.

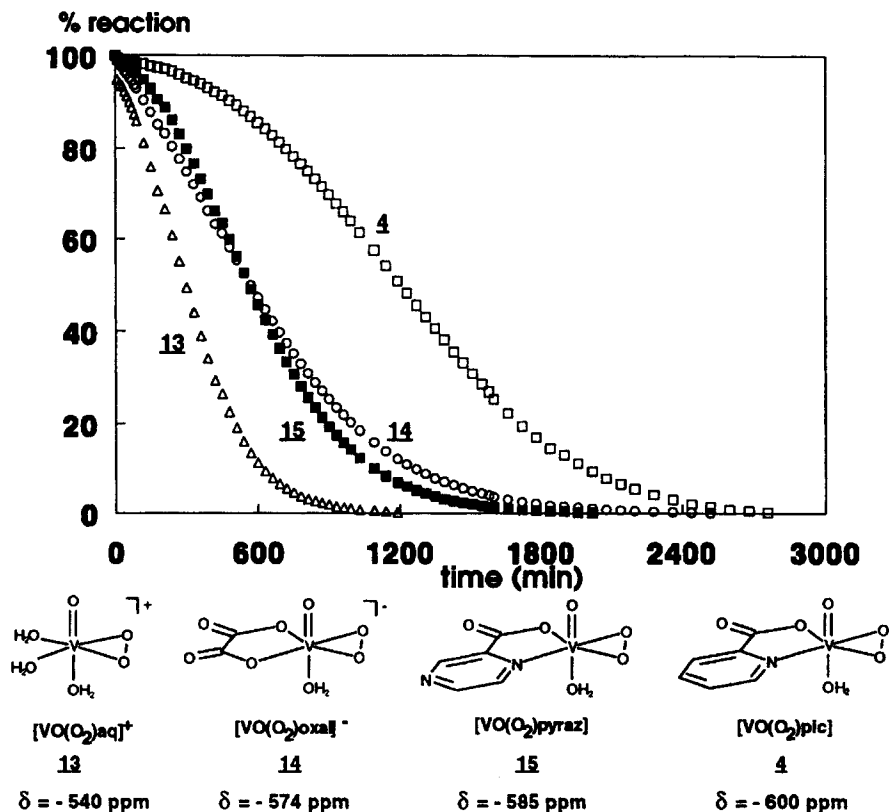


Figure 4. Disappearance of the oxidant as a function of the time, measured by the decrease of the absorbance at the λ_{\max} values, in the decomposition reactions of 0.005 mol L^{-1} of (▽) $[\text{VO}(\text{O}_2)\text{aq}]^+$ (13), (○) $[\text{VO}(\text{O}_2)\text{oxal}]^-$ (14), (■) $[\text{VO}(\text{O}_2)\text{pyraz}]$ and (□) $[\text{VO}(\text{O}_2)\text{pic}]$ (4) in water (HClO_4 , pH1) at 37°C

more complicated than a simple electronic effect so that all the predictions must be considered with great care until a better knowledge of the various processes is available.

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