

Review

From polyoxometalates to polyoxoperoxometalates and back again; potential applications

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Dedicated to Professor Paulette Herpin.

Abstract

This short review is concerned with sustainable chemistry and recent research progress in catalysis systems for the use of aqueous hydrogen peroxide or dioxygen. Some achievements in the development of catalysts for epoxidations and for carbon–carbon bond cleavage are presented. Special emphasis is placed on fully inorganic systems, some with the dimeric moiety $[M_2O_2(\mu-O_2)_2(O_2)_2]$, ($M = V, Mo, W$) which have more scope than those containing organic ligands or supports, however robust. Oxoperoxometalate species with or without assembling ligands can be used for homogeneous, two-phase and phase-transfer catalyses and to prepare mesoporous materials (M-MCM-41, M-SBA-15, etc.) and supported catalysts for effective immobilization of activated metal peroxo complexes. Moreover, the decomposition of molybdenum and vanadium oxoperoxo species in water and phosphoric acid leads to an elegant method for preparing $H_{3+n}[PMo_{12-n}V_nO_{40}] \cdot aq$ ($n = 2-9$) at room temperature, avoiding the tedious synthesis with diethyl ether extraction. Spectrometric, structural and reactivity data on the precursor complexes lead to a more rational approach to catalysis systems and to the discovery of novel classes of precursors and/or catalysts for the selective transfer of oxygen to organic substrates.

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Keywords: Catalysis; Dioxygen; Hydrogen peroxide; Oxidation; Peroxo ligands

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1. Introduction

Selective and partial oxidation reactions are some of the most useful processes in synthetic organic chemistry. Percarboxylic acids present serious safety problems for large-scale production and they leave acid waste. Apart from alkyl hydroperoxides, for which elegant recycling reactions of alkoxides and alcohols have been developed [1] and dioxygen, hydrogen peroxide is the most benign and low-waste reagent for oxidations. It is important to find highly effective catalytic methods for activating aqueous and non-aqueous hydrogen peroxide systems and also for preparing it more safely. Transition metal (TM) polyoxoperoxo systems can be regarded as inorganic catalytic analogues of peracids; as such they have potential applications in replacing percarboxylic acids.

Polyoxometalates (POMs) and polyoxoperoxo-metalates (POPOMs) are members of the large class of oxidants and are amongst the most important for activating hydrogen peroxide. Key precursors or catalysts include the well-known Keggin dodecatungsto(or molybdo)-phosphate anion (Fig. 1) [2], the mononuclear neutral oxo-di-(η^2 -peroxo) species with chromium(VI) [3,4], molybdenum(VI) [5,6], tungsten(VI) [7] and rhenium(VII) [8]. These complexes: $[\text{CrO}(\text{O}_2)_2\text{py}]$, $[\text{MO}(\text{O}_2)_2\text{LL}']$, ($\text{M}=\text{Mo}, \text{W}$ and $\text{L}=\text{H}_2\text{O}$, $\text{L}'=\text{hmpa}$ or $\text{L}=\text{L}'=\text{pyO}$) and $[\text{MeReO}(\text{O}_2)_2]$ (Fig. 2) inspired research to make use of hydrogen peroxide via selective heterolytic processes. Very exciting developments were also the synthesis and characterization of tetranuclear complexes which contain an assembling ligand (e.g. phosphate, arsenate, sulfate, etc.) “(AmH)H₂[PO₂(Mo₂O₁₁)₂·2Am]” (Am = 2-aminopyridine) [9], reformulated as (AmH)₃[PO₄{Mo₂O₂(μ -O₂)₂(O₂)₂}₂] [10] after the discovery of analogues with tungsten(VI), the so-called Venturrello complex [11], and with molybdenum(VI) [10].

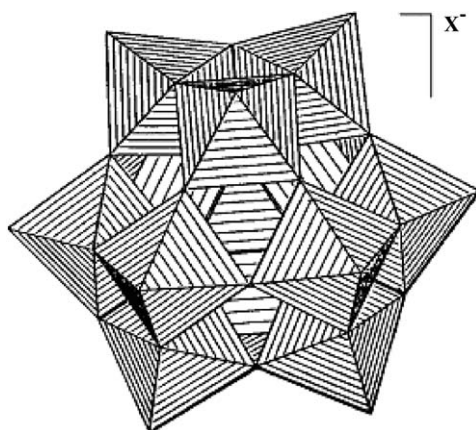


Fig. 1. The Keggin structure of the $[\text{XM}_{12}\text{O}_{40}]^{\text{X}-}$, where X is the central atom, X = Si(IV), P(V), Ge(IV), etc., M = Mo(VI), W(VI), etc.

Keggin heteropolyanions have been used by several groups for mild and selective oxidations with hydrogen peroxide [12–16]. Many of them are often only precursors of the true catalysts; their lack of solvolytic stability in aqueous hydrogen peroxide was attributed to equilibria between Keggin and lacunary heteropolyanions plus $\{\text{MO}_2\}^{\text{+ or 2+}}$ or $\{\text{MO}_2(\text{OH})\}^{\text{x+}}$ species, ($\text{M}=\text{V}, \text{Mo}, \text{W}$, etc. $x=0$ or 1) [17,18]. These mononuclear groups can subsequently react with H_2O_2 to generate the Mimoun-like species $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$, $[\text{WO}(\text{OH})(\text{O}_2)_2]^-$ and $[\{\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})\}_2(\mu\text{-O})]^{2-}$, ($\text{M}=\text{Mo}, \text{W}$), etc. All these oxoperoxo complexes can ligate assembling anions ($[\text{PO}_4]^{3-}$, $[\text{AsO}_4]^{3-}$, $[\text{SO}_4]^{2-}$, $[\text{R}_2\text{SiO}_2]^{2-}$, $[\text{R}_3\text{SiO}]^-$, etc.) thus forming mono- to tetranuclear anionic species (vide infra). As shown in several papers and patents, the dinuclear μ -oxo aqua-anion is a preferred catalyst for oxidation of hydrophilic substrates in water [19].

With $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot \text{aq}$, more drastic conditions (70% H_2O_2 in water, $[\text{H}_2\text{O}_2]/[\text{W}] \simeq 8000$) have to be used to degrade the Keggin type polyanionic structure [10,20–22]. This observation has to be correlated with the stability of silicotungstates in water as compared to phosphotungstates [23]. As a counterpart, systematic studies focus on hydrogen peroxide-based epoxidation catalysed by lacunary polyoxometalates [24], e.g. $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$. On the other hand, new lacunary heteropolyoxotetraperoxo-tungstates, related to the Keggin structure, have been proposed for oxidations; for example, $[(\text{Co}^{\text{II}}\text{O}_4)\text{W}_{11}\text{O}_{31}(\text{O}_2)_4]^{10-}$ has been characterized by single-crystal X-ray diffraction [25]. The authors underlined that the reactivities of the lacunary complexes towards aqueous H_2O_2 may be related to the longer $\text{W}=\text{O}$ bonds of the terminal oxygen atoms of *cis*- $\text{W}(\text{O})_2$ groups around the vacancy leading to *cis*- $\text{WO}(\text{O}_2)$.

The non-lacunary heteropolyoxoperoxo-metalates $[\text{PTiW}_{11}\text{O}_{39}(\text{O}_2)]^{5-}$ and $[\text{PTi}_2\text{W}_{10}\text{O}_{38}(\text{O}_2)_2]^{7-}$ have also been reported [26,27]. In these compounds, the peroxo ligands are probably bonded to the titanium atom (but statistical disorder makes it impossible to locate the Ti atoms and the peroxo ligands). These substituted polyoxometalates are

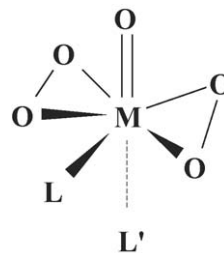
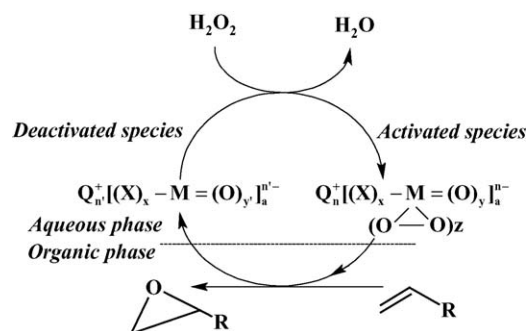


Fig. 2. Mononuclear oxodiperoxo complexes ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$; $\text{L}=\text{L}'=\text{H}_2\text{O}$; $\text{L}=\text{H}_2\text{O}$, $\text{L}'=\text{hmpa}$, etc.; $\text{M}=\text{Re}$, $\text{L}=\text{Me}$, $\text{L}'=\text{H}_2\text{O}$; etc.) (hmpa = hexamethylphosphoric triamide).



Scheme 1. Principle of phase-transfer catalysis with anionic oxoperoxo species and onium salts. ($X = \text{EO}_4$ with $E = \text{P(V)}$, As(V) , etc. or ZYEO_2 ; Q^+ = onium cation). (see text and Table 2).

moderately active for olefin epoxidation using 30% H_2O_2 ($\text{O}_{\text{peroxo}}/\text{catalyst} = 1200:2$ mol/mol). It is inferred that there is no degradation of the Keggin-structured framework at 50°C in 24 h [27], although synergy may exist between the tungsten and titanium centres. The retention of the structure of the Keggin unit of this Ti-POM was reinvestigated [28], but we must bear in mind that in some systems the isolable species are often not those that lie along the principal reaction coordinates for catalysis [17,18,29].

Another interesting set of precursors includes, for example, $\{[\text{WZn}(\text{TM})_2(\text{H}_2\text{O})_2]\{\text{ZnW}_9\text{O}_{34}\}_2\}^{12-}$ salts (in which a transition metal, typically $\text{TM} = \text{Mn(II)}$, Zn(II) , etc. replaces an $\text{W}=\text{O}$ moiety at the POM surface). They were thoroughly studied for the selective epoxidation of allylic alcohols [30] and of many other substrates [31–33] with hydrogen peroxide. Tungsten oxoperoxo complexes rather than high-valent transition-metal-oxo species operate as the active intermediates in these systems, and have to be identified. Comparative studies of the known systems are of interest but optimization of conversion and selectivity is not easy: all these catalysed oxidation reactions are carried out in a homogeneous system, or in two-phase systems, or even by phase-transfer catalysis (PTC) (Scheme 1). High selectivities are usually obtained with the two heterogeneous systems, but several parameters must be considered: the effects of solvent(s), of the concentrations, of the nature of the cation(s) Q^+ (onium species, the length of the alkyl groups partly determines the extraction efficiency), of the assembling ligand X , of all the anions, of the pH of the aqueous phase, of the presence of Na^+Cl^- (“brine effect” which modifies the distribution of the species) and of the $\text{M}:\text{X}:\text{Q}^+$ ratios, etc. Some anionic complexes with the dimeric moiety $\{\text{M}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}$, as a principal building block are better, for the transfer of active oxygen, than mononuclear species which are much less active. The combination of these anions with appropriate cations is claimed to be as active and selective as the two-phase systems: “ MeReO_3 (MTO)/ H_2O_2 - H_2O /organic solvent” [17,34–37] particularly effective for the epoxidation of acid-sensitive epoxides. The addition of “proton sponges” (e.g. bipyridine or preferably 2,2'-bipyridyl- N,N' -dioxide, etc.) is useful to prevent side reactions and hence improve epoxide selectivity [17,36].

We have chosen not to discuss all the innovations, but only those related to a particular set of active and structurally

well defined anionic oxoperoxo metalates: (i) the tetranuclear onium salts with $\mu_2\text{-}\eta^2\text{:}\eta^1$ peroxo ligands $\text{Q}_3[\text{EO}_4\{\text{M}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}_2]$ denoted “ PM_4 ” or “ AsM_4 ” if $E = \text{P(V)}$ or As(V) , $\text{M} = \text{Mo(VI)}$, W(VI) or V(V) , and Q^+ = onium cation; (ii) parent dinuclear salts: $\text{Q}_2[\text{ZYEO}_2\{\text{M}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}]$ with $E = \text{P(V)}$, As(V) , S(VI) , Si(IV) , etc. and Z , $\text{Y} = \text{OH}$, O , Ph , Me , $i\text{-Bu}$, CH_2Cl , etc. Mono- and trinuclear species will be briefly considered as well as more detailed information about the relations between POPOMs or “ EM_n ” and POMs with special emphasis on the development of novel syntheses of solid catalysts based upon these anionic species.

2. Tetranuclear onium salts with $\mu_2\text{-}\eta^2\text{:}\eta^1$ peroxo groups

A major breakthrough was the discovery of complexes with $\{\text{M}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}$ moieties [9–11]. They were synthesized from $\text{MO}_3\cdot\text{H}_2\text{O}$ or $[\text{MO}_4]^{2-}/[\text{PO}_4]^{3-}/\text{H}_2\text{O}_2\text{-H}_3\text{O}^+\text{-H}_2\text{O}/\text{Q}^+$ systems. It was suggested [21] and then convincingly proved [10,20,22], that the Keggin dodecatungsto-(or molybdo)-phosphate anion of $\text{H}_3[\text{PM}_{12}\text{O}_{40}]\cdot\text{aq}$ with aqueous H_2O_2 , at the origin of many papers and patents (for example Rassat and Ishii’s systems), was decomposed to give the true catalyst complexes (e.g. with $\text{M} = \text{W}$ ca. “ PW_4 ”, “ PW_3 ”, “ PW_2 ”, “ PW_1 ” and $[\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2(\mu\text{-O})]^{2-}$). These results were supported both by the isolation of the corresponding anionic complexes, solution spectroscopic studies (UV, IR, Raman, ^{31}P and ^{183}W NMR spectroscopy) and by X-ray diffraction on single crystals. The instability of another Keggin-type heteropolyanion in the presence of aqueous hydrogen peroxide was also reported recently [38]: $\text{HN}_{12}[\text{AsW}_{12}\text{O}_{40}]$ is mainly degraded to $[\text{AsO}_4\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}_2]^{3-}$, $[\text{HASO}_4\{\text{W}_2\text{O}_2(\mu\text{-O})_2(\text{O}_2)_2\}]^{2-}$ which is the first structurally characterized example of an arsenic(V)-containing polyoxoperoxo metalate, and $[\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2(\mu\text{-O})]^{2-}$. It was shown that “ PW_4 ” and “ PW_2 ”, which have no coordinated water, are mainly responsible for the catalytic activity of phase-transfer systems involving $\text{H}_3[\text{PW}_{12}\text{O}_{40}]/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{organic solvent/alkene}$ and lipophilic onium cations [20–22,39,40], though anhydrous mono- and dinuclear tungsten peroxo species may contribute. Subsequent reactions to produce diols from epoxides and even carbon–carbon bond cleavage can be suppressed, resulting in a very high selectivity for epoxidation at room temperature [34,37,38]. With hydrophilic substrates the alkaline salts of $[\{\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2(\mu\text{-O})]^{2-}$ are preferred, as shown in several papers [41,42], the results depending on the hydrophobic/hydrophilic balance. All investigations on the identity of the active species under Venturello’s conditions ($[\text{MO}_4]^{2-}/[\text{PO}_4]^{3-}/[\text{H}_3\text{O}^+]/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{phase-transfer catalyst (PTC)}/\text{organic solvent}/60^\circ\text{C}$) [11] and under Ishii’s conditions ($\text{H}_3[\text{PM}_{12}\text{O}_{40}]\cdot\text{aq}/\text{H}_2\text{O}_2\text{-H}_2\text{O}/\text{PTC}/\text{organic solvent}/40\text{--}70^\circ\text{C}$) [15,16], ($\text{M} = \text{Mo}$ or W) indicate that the two catalysis systems involve common oxoperoxo anions, despite the fact that each group patented its particular set of catalyst precursors as novel chemistry. These systems, nevertheless, can differ in the concentration ratios of the neutral and anionic species. Worth noting also is the use of H_2O_2 to decompose isopolymetalates

Table 1

Tetranuclear complexes, structurally related to PW_4 , of general formula $Q_n[EO_4\{M_2O_2(\mu-O)_2(O_2)_2\}_2]$ with references to crystal structures (see Fig. 3)

E	M	Q^+	n	Ref.
P	W	$[(n\text{-Hex})_4N]^+$	3	[11]
P	Mo	$[(n\text{-Hex})_4N]^+$	3	[10]
As	W	$[(n\text{-Hex})_4N]^+$	3	[38]
P	V	$[NH_4]^+$	7	[44]

such as $[Nb_6O_{19}]^{8-}$ [43], paratungstate $[H_2W_{12}O_{42}]^{10-}$, and heptamolybdate $[Mo_7O_{24}]^{6-}$, etc. into low-nuclearity oxoperoxo species [20,21]. In other words, it is to be emphasized that many POMs can lose their polyanionic structure in the presence of excess hydrogen peroxide; additional work on POMs as oxidation pre-catalysts is needed.

Complexes that are structurally related to “ PW_4 ” are summarized in Table 1. X-ray analyses show that the molybdenum and the two tungsten complexes are isomorphous, and that the four anions are structurally very similar. The anions (Fig. 3) consist of a slightly distorted tetrahedral assembling anion $[EO_4]^{3-}$ and two neutral units, $\{M_2O_2(\mu-O)_2(O_2)_2\}$ in which the M(VI), (M=Mo or W) or V(V) atoms are seven-coordinated by oxygen atoms in a pentagonal bipyramidal arrangement (Fig. 3). The four oxygen atoms of the $[EO_4]^{3-}$ anion are corner-sharing with the basal planes of the four different pentagonal bipyramids. The metal centres have two peroxo ligands, one in a η^2 -side-bound configuration, the other in the μ_2 - η^2 : η^1 mode (or bridging unsymmetrical). One of the axial positions is occupied by a terminal oxo ligand O^{2-} and the other by an oxygen atom of a bridging unsymmetrical peroxo group with notably long bonds (2.30–2.40 Å). This can favour fluxionality [17,18,29] in two-phase systems (see Section 6) as well as in many solvents.

Tetranuclear polyoxoperoxometalates anions are not unique but, to the best of our knowledge, species containing μ_2 - η^2 : η^1 peroxo moieties are active oxidation catalysts with H_2O_2 , while species which contain only η^2 -peroxo linkages (Fig. 4) such as $[W_4O_6(O_2)_6(OMe)_2(MeOH)_2]^{2-}$ [45], $[W_4O_6(O_2)_6(OH)_2(H_2O)_6]^{2-}$ [46], etc. are not, nor is the unprecedented tetranuclear polyoxoperoxometalate anion: $[M_4O_{12}(O_2)_2]^{4-}$, with M=Mo, W where each metal atom is surrounded by six oxygen atoms to form a distorted MO_6 octahedron (Fig. 5) [47,48]. The two μ_4 -peroxo groups link a neutral M_4O_{12} moiety (see Fig. 5). The potassium salt,

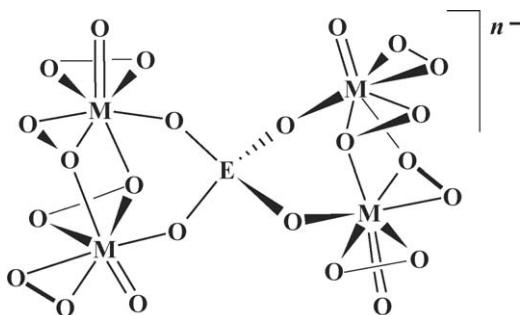


Fig. 3. Structure of tetranuclear polyoxoperoxometalate anions $[EO_4\{M_2O_2(\mu-O)_2(O_2)_2\}_2]^{n-}$ with μ_2 - η^2 : η^1 peroxo ligands (see Table 1).

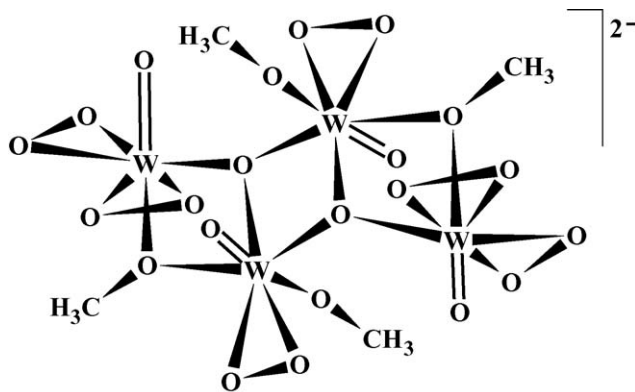


Fig. 4. Anionic structure of $[W_4O_6(O_2)_6(OMe)_2(MeOH)_2]^{2-}$, see ref. [45].

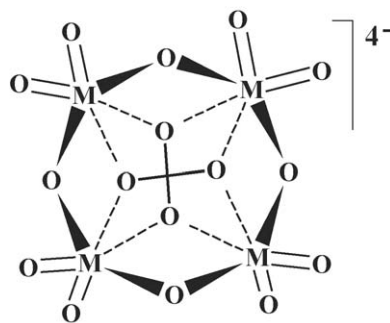


Fig. 5. An unprecedented tetranuclear polyoxoperoxometalate anion: $[M_4O_{12}(O_2)_2]^{4-}$, (M=Mo, W) (see text and ref. [47,48]).

$K_6[Mo_5O_{10}(O_2)_8] \cdot 5H_2O$, is such that the anion may be visualized as being formed from two $[\{MoO(O_2)_2\}_2(\mu-O)]^{2-}$ with $[MoO_4]^{2-}$ as an assembling anion in which four Mo(VI) atoms are seven-coordinated by oxygen atoms in a pentagonal bipyramidal arrangement and one Mo(VI) with tetrahedral coordination. This configuration has no tridentate μ_2 - η^2 : η^1 - O_2^{2-} , but eight bidentate η^2 - O_2^{2-} [49]. Therefore, replacing $[MoO_4]^{2-}$ by $[PO_4]^{3-}$ or $[AsO_4]^{3-}$ leads to different structural types.

3. Dinuclear onium salts with μ_2 - η^2 : η^1 peroxo groups

Many data were obtained on different oxoperoxo complexes without a tridentate peroxo group, particularly the “tetraperoxotrimolybdate” ion, $[\{MoO(O_2)_2\}_2(\mu-MoO_4)(\mu-O)]^{4-}$ from Trysberg and Stomberg [50], but new developments greatly extend the scope of possible oxidations with peroxo systems: discovery of titanium silicalite (TS-1), enantioselective syntheses of epoxides, “ $MeReO_3$ (MTO)/ H_2O_2 - H_2O /organic solvent” systems, and PW_n complexes, etc. [17]. With PW_n , the existence of nuclear spins $I=1/2$ from ^{31}P and ^{183}W favours a systematic reinvestigation of oxidations using tungsten-based precursors considered a long time ago [12,13,15]: “ $H_3[PW_{12}O_{40}] \cdot aq$ or H_2WO_4/H_3PO_4 and H_2O_2/H_2O ”. From an acetonitrile solution of the tetra-*n*-butylammonium salt corresponding to “ PW_4 ” [20,21], the ^{31}P NMR line ($\delta=+4.2$ ppm), flanked

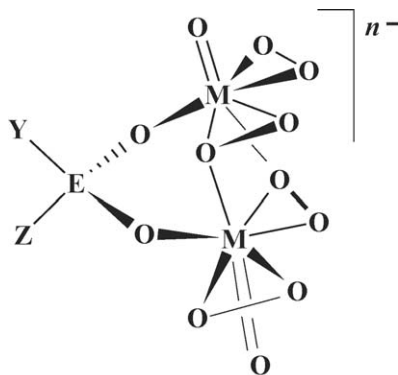


Fig. 6. Structure of dinuclear polyoxoperoxometalate anions $[ZYEO_2\{M_2O_2(\mu-O)_2(O_2)_2\}]^{n-}$ with $\mu_2-\eta^2:\eta^1$ peroxo ligands (see Table 2).

by well resolved satellites arising from isotopomers, confirms that the $[PO_4]^{3-}$ group is surrounded by four equivalent tungsten atoms, as in the solid state ($^2J_{W-O-P} = 18.5$ Hz). In addition, the ^{183}W spectrum consists of a doublet at $\delta = -593$ ppm, $^2J_{W-O-P} = 18.5$ Hz. The formation of other intermediate species was also found [22,39,45] and their subsequent characterization led to detailed knowledge on several tungsten POM/ H_2O_2 - H_2O or $H_2WO_4/[PO_4]^{3-}/H_2O_2$ - H_2O systems by ^{31}P and ^{183}W NMR. Novel signals have been assigned to new phosphate-oxoperoxotungstate species: $[PW_4O_{24}]^{3-}$, $[PW_3O_m]^{2-}$, $[PW_2O_p]^{1-}$ and $[PWO_q]^{0-}$; the coupling constants $^2J_{W-O-P}$ are significantly different and decrease with the number of tungsten atoms (25.0, 24.4, 23.0, 22.3 Hz, respectively) while δ values increase (-3.5 , -1.5 , -0.3 , $+0.3$ ppm). This allowed to correlate the ^{31}P signals with the three ^{183}W NMR doublets between -660 and -680 ppm. These NMR studies led to the isolation of all the previously unknown species as onium salts.

We focused our efforts on dinuclear complexes because structural data (X-ray, IR and Raman) reveal an asymmetric peroxo group, which may facilitate oxygen transfer (Fig. 6). Since the

Table 2
Dinuclear complexes, structurally related to PW_2 , of general formula $Q_n[ZYE O_2\{M_2O_2(\mu-O)_2(O_2)_2\}]$ with references to crystal structures (see Fig. 6)

E	Y	Z	M	Q^+	n	Ref.
P	OH	O	W	$[(n-Bu)_4N]^+$	2	[22]
As	OH	O	W	$[(n-Bu)_4N]^+$	2	[51]
As	Me	O	W	$[(n-Bu)_4N]^+$	2	[51]
P	OH	O	V	$[NH_4]^+$	5	[52]
S	O	O	Mo	$[(n-Bu)_4N]^+$	2	[53]
S	O	O	W	$[(n-Bu)_4N]^+$	2	[53]
P	Ph	O	W	$[(n-Bu)_4N]^+$	2	[54]
P	Ph	Ph	W	$[(n-Bu)_4N]^+$	1	[55]
P	Ph	Ph	Mo	$[Me_4N]^+$	1	[55]
As	Me	Me	Mo	$[Me_4N]^+$	1	[55]
Si	Ph	Ph	Mo	$[PPh_4]^+$	2	[56]
Si	Ph	Ph	W	$[PPh_4]^+$	2	[56]
Si	Me	Me	Mo	$[PPh_4]^+$	2	[57]
Si	<i>i</i> -Bu	<i>i</i> -Bu	Mo	$[PPh_4]^+$	2	[57]
Si	Me	CH_2Cl	Mo	$[PPh_4]^+$	2	[57]

discovery of this structural feature, several groups have prepared parent complexes (Table 2), some of them being proposed for industrial use [17] (vide infra). It is possible to attach XW_2 as well as XW complexes covalently to solid supports (vide infra). Moreover, an unusual effect of the assembling ligand(s) has been found: the dinuclear complexes containing sulfato anions [53] are among the most efficient for the transfer of active oxygen to olefinic substrates at room temperature under stoichiometric conditions but can only be regenerated in highly acidic media (H_2O_2 - H_2O - H_2SO_4); otherwise a poorly active trinuclear precursor is formed (vide infra).

4. Parent trinuclear heteropolyoxoperoxo complexes and mononuclear species

Trinuclear heteropolyoxoperoxo complexes were also evidenced by ^{31}P and ^{183}W NMR [22,39,45] (vide supra), and some of them were isolated and their crystal structures reported [46], for example, with molybdenum(VI): $[NMe_4]_2[(PhPO_3)\{Mo_2O_2(\mu-O)_2\}\{MoO(O_2)_2(H_2O)\}]$. Another trinuclear species is $[NMe_4][\{(Ph_2PO_2)_2\}\{WO_2(O_2)_2\}\{WO(O_2)(OH)(OH_2)\}]\cdot EtOH\cdot H_2O\cdot 0.5$ MeOH.

The tungsten moieties are linked via two μ -oxo, a μ_3 -oxo and two diphenylphosphinate ligands. The peroxide ligands are side-bonded [58]. At present, they are considered as weakly active precursors for PTC (NMe_4^+ salts and the length of the alkyl groups partly determine the extraction efficiency, presence of OH^- and H_2O , ...). Several groups were inspired to consider sulfate-based systems.

The compounds $[Me_4N]_3[(HSO_4)(SO_4)\{(W_3O_6)(O_2)_3\}]\cdot 3.5H_2O$ and $[Me_4N]_3[(HSO_4)(SO_4)\{(Mo_3O_6)(O_2)_3\}]\cdot 3H_2O$ were isolated from the reaction of strongly acid solutions (sulfuric acid + molybdate or "tungstic acid", $WO_3\cdot H_2O$). They have a side-on peroxo group on each metal centre; the bridging ligands are oxo, sulfato and hydrogenosulfato groups [53,59]. These results complement a previous study [60] devoted to the synthesis and X-ray structure determination of $[Me_4N]_4[\{(HSO_4)(W_3O_7)(O_2)_2\}_2O]$.

Novel mononuclear anionic species have also been synthesized; inevitably they are anionic analogues of Stomberg/Mimoun/Herrmann-type molecular complexes, containing only η^2 -peroxo groups. Thus, the mononuclear complexes $[NH_4][\{(Ph_2PO_2)\}\{MO(O_2)_2(H_2O)\}]$ with two η^2 -peroxo groups are even poorer catalysts than the dinuclear species with Ph_2PO_2 [55]. $WO_3\cdot H_2O$ [or $MoO_3\cdot H_2O$] reacts with 30% hydrogen peroxide following addition of Ph_3SiOH or $[\{Ph_2SiOH\}_2O]$, affording mono- or dimeric peroxo compounds $[Ph_3SiO\{MO(O_2)_2\}]^-$ or $[\{(Ph_2SiO)\}\{MO(O_2)_2\}_2O]^{2-}$ which were isolated as PPh_4^+ salts [61] (Fig. 7). These six-coordinate, pentagonal monopyramid with symmetrically bound peroxo-ligands and a vacant site trans to the oxo group are structurally unique, as is $[\{Ph_3SiO\}_2V^VO(O_2)]^-$ with a geometry at the metal ion which is described as a trapezoidal pyramid (Fig. 7). This has been characterized in a mixed-crystal compound, $[PPh_4][\{Ph_3SiO\}_2VO_2]_x[\{Ph_3SiO\}_2VO(O_2)]_{1-x}$ where $x=0.57$. The $[VO(O_2)]^+$ core is derived from the monoperoxovanadate cation; it provides a coordination number,

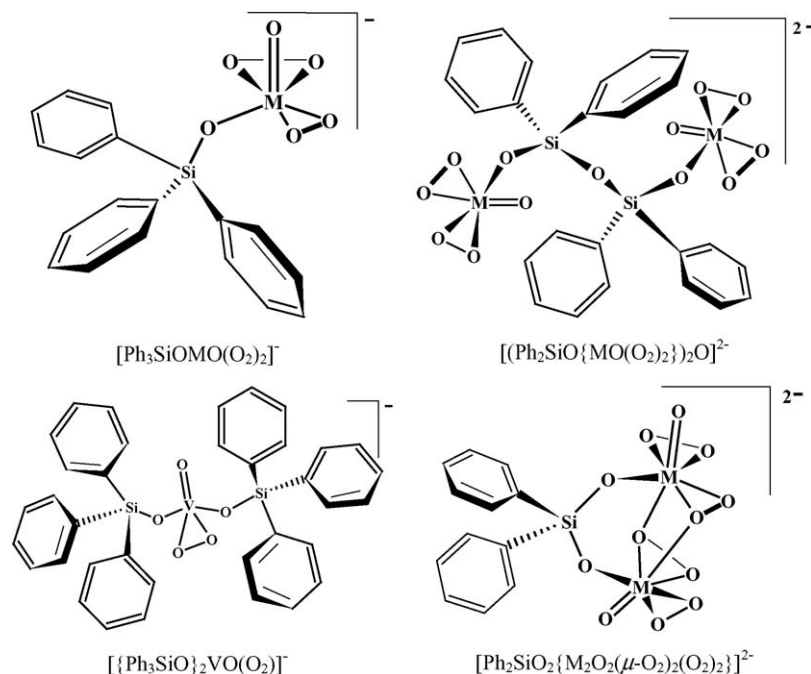


Fig. 7. The first structurally characterized examples of silicon-containing polyoxoperoxometalates (M = Mo, W) [56,61,62].

and even an arrangement around vanadium, which is close to that found in V-chloroperoxidase in *Curvularia inaequalis* (peroxygen form) [62]. Vanadium oxohydroperoxo complexes are possible intermediates for the recently proposed system with $[\gamma\text{-}1,2\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$ having the $\{\text{OV}(\mu\text{-OH})_2\text{-VO}\}$ core which catalyses epoxidation of olefins using only one equivalent of H_2O_2 with high efficiency in MeCN/*t*-BuOH/ H_2O_2 mixtures [63]. We shall consider now some of the most common anionic species for preparing mixed Keggin-type anions with molybdenum(VI) and vanadium(V).

5. A “peroxo route” for preparing heteropolyacids mixtures of general formula “ $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}] \cdot \text{aq}$ ” denoted HPA-*n* (back again)

HPA-*n* catalysts are commonly prepared by the reaction of sodium molybdate and sodium metavanadate with Na_2HPO_4 under acidic conditions (concentrated H_2SO_4 or HCl). In our hands the yields are lower than 40% after the tedious and dangerous, on a large scale, diethyl ether extractions [64]. The method is limited to $n=1, 2$ or 3. Other routes [65] with $\text{V}_2\text{O}_5/\text{H}_3\text{PO}_4/\text{MoO}_3 \cdot \text{H}_2\text{O}$ have not been extended to $n > 2$. In this case, V_2O_5 must have a high specific surface area to avoid long reaction times. HPA-*n* catalysts can also be prepared by combinatorial methods from two stock solutions of different building blocks as oxoperoxo species [66,67]. The oxoperoxo-vanadium and molybdenum complexes are attractive precursors for several reasons. They are practical reagents for vanadium(V) and molybdenum(VI) because their counter-ions are H^+ (or OH^-). There are, therefore, no undesired species such as chloride, nitrate, ammonium or sodium (vide supra) to keep

crystallization or heat treatment under control or to remove before heat treatment. We showed that $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$, $[\{\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})\}_2(\mu\text{-O})]^{2-}$, “ PMo_4 ” and even “ PMo_2 ” prepared at room temperature, can be used to prepare HPA-*n* with vanadium oxoperoxo analogues such as $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})_3]^+$ (the predominant monoperoxo-vanadate cation species at $\text{pH} \approx 1$), $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})_2]^-$ (the diperoxo-vanadate anion formed at 0°C and at $\text{pH} \approx 3$, in the presence of additional hydrogen peroxide). The $[\text{PO}_4]^{3-}$ /molybdenum(VI)/vanadium(V) ratios can be adjusted in the range 1:10:2 to 1:3:9 [66,67]. The ease of the vanadium(V)/vanadium(IV) redox-step introduces a mixture of two-electron and one-electron character into vanadium oxoperoxo chemistry, which is responsible for free-radical character into its reaction, via decomposition of the peroxo species and possible formation of a $\text{V}^{\text{IV}}\text{-OO}$ moiety. Dioxygen is used to oxidize vanadium(IV) back in the presence of a slight excess of H_3PO_4 , as in the reactions of HPA-*n* in catalytic systems for the carbon–carbon bond cleavage of ketones and of α -ketols [17]. Finally, the above-mentioned peroxo route gives pure Brönsted acids (see Fig. 8b vide infra) with low H_3PO_4 content. Solid products are obtained by slow evaporation at room temperature. They can be examined by TG, DTA, powder X-ray diffraction, IR and UV–vis spectroscopy, ^{31}P and ^{51}V NMR spectroscopy [66–68]. In all cases, HPA-*n* ($n=2\text{--}9$) corresponds to a mixture of products and of isomers; the activity of the mixture is partly due to the presence of $[\text{VO}_2]^+$ [17,68,69], to the fast equilibria between the labile species ($[\text{VO}_2]^+$ and lacunary HPA-*n*) and those between dioxygen with the reduced forms “ $\text{H}_{i+3+n}[\text{PMo}_{12-n}^{\text{VI}}\text{V}_{n-i}^{\text{V}}\text{V}_i^{\text{IV}}\text{O}_{40}] \cdot \text{aq}$ ”, denoted $\text{H}_i[\text{HPA-}n]$ (Scheme 2). The process has been used by several groups (see, for example, [17,69,70]).

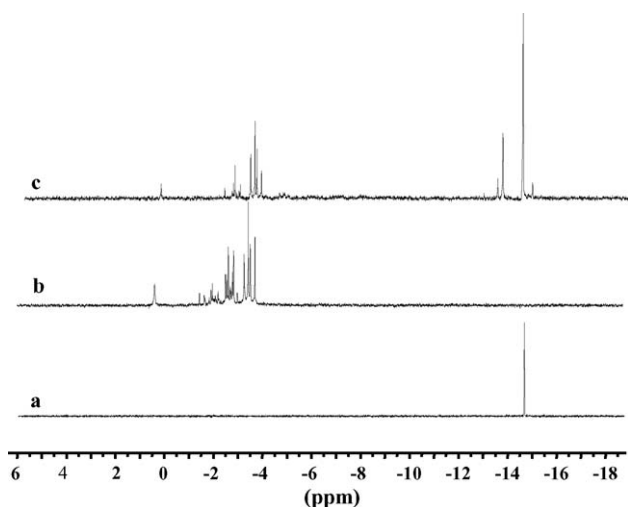
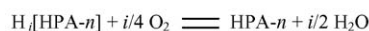
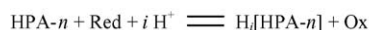
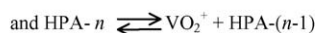


Fig. 8. ^{31}P NMR spectrum of: (a) $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot\text{aq}$, ca. 0.1 M; (b) $\text{H}_3[\text{PMo}_9\text{V}_3\text{O}_{40}]\cdot\text{aq}$, ca. 0.1 M; (c) mixture of the two solutions; the spectrum was recorded 20 nm after preparation of the solution (solvent $\text{D}_2\text{O}/\text{H}_2\text{O}$ 1/1, $T=297\text{ K}$).



Where $\text{H}_i[\text{HPA-}n]$ denotes " $\text{H}_{i+3-n}[\text{PMo}^{\text{VI}}_{12-n}\text{V}^{\text{V}}_{n-i}\text{V}^{\text{IV}}_i\text{O}_{40}]\cdot\text{aq}$ "



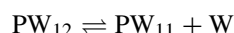
Scheme 2. Mass balance $\text{HPA-}n/\text{O}_2/\text{H}^+$ for redox processes.

6. Molybdenum(VI)/vanadium(V)/tungsten(VI) interchange of heteropolyanions with the Keggin structure and the counterpart with oxoperoxo species having $\mu_2\text{-}\eta^2\text{:}\eta^1$ peroxy groups

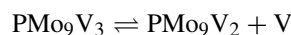
Molybdenum(VI)/tungsten(VI) interchange was shown by ^{31}P NMR: after 1 h at 20°C , a solution of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\cdot\text{aq}$ and $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot\text{aq}$ in water (each $1.33 \times 10^{-2}\text{ mol l}^{-1}$) give a ^{31}P NMR spectrum with 13 complex signals in the -14 to -5 ppm range [71]; they are attributed to the mixed-metal isomers $[\text{PMo}_n\text{W}_{12-n}\text{O}_{40}]^{3-}$ which have been used independently

as precursors with aqueous H_2O_2 [72]. In aprotic organic solvents, such an exchange between different HPAs with these Keggin structures is not observed. We proposed that the exchanged species in water is due to $\{\text{MO}_p\}^{x+}$ or $\{\text{MO}_2(\text{OH})\}^+$ groups ($\text{M}=\text{Mo}$ or W). Exchange of these structural units has not been directly observed, although we suggest that it may be mainly responsible for the ^{18}O (or ^{17}O)-water/ ^{16}O -HPA exchange observed by several groups [2,73,74].

Upon combining " $\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]\cdot\text{aq}$ " with $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot\text{aq}$ in an aqueous solution, similar changes in the ^{31}P NMR spectra occur (Fig. 8). From the stepwise appearance of new signals it seems likely that exchange takes place by single $\{\text{MO}_p\}^{x+}$ or $\{\text{MO}_2(\text{OH})\}^+$ units only, giving subsequent formation of mixed species in the Keggin series. The following equilibria represent these observations:



⋮



⋮



where "W" and "V" are mononuclear oxohydroxo moieties (vide supra). Addition of H_2O_2 itself promotes the formation of mononuclear oxodiperoxo species $\{\text{MO}(\text{O}_2)_2\}^{-1\text{ or }0}$, which are involved in other mechanistically important equilibria involving several complexes. We observed that onium salts of the tetranuclear oxoperoxo anions, $[\text{PO}_4\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{3-}$, ($\text{M}=\text{Mo}$ and W and even V) are also in equilibrium with the $\{\text{MO}(\text{O}_2)_2\}$ moiety, leading again to a redistribution process (see Fig. 9), with the formation of three mixed-addenda species $[\text{PO}_4\{\text{Mo}_{(4-x)}\text{W}_x\text{O}_{24}\}]^{3-}$, denoted " $\text{PW}_{4-x}\text{Mo}_x$ ", ($x=1\text{--}3$). The four inner oxygen atoms surrounding the phosphorus(V) do not exchange under these conditions. Therefore, there is no rapid chemical exchange between free phosphate and $\{\text{MO}(\text{O}_2)_2\}^{-1\text{ or }0}$ moiety for POPOMs or $\{\text{MO}_2(\text{OH})\}^+$ species for POMs. One of the differences between the two types of anion is the existence of fluxionality for the inorganic oxoperoxo complexes, which was attributed

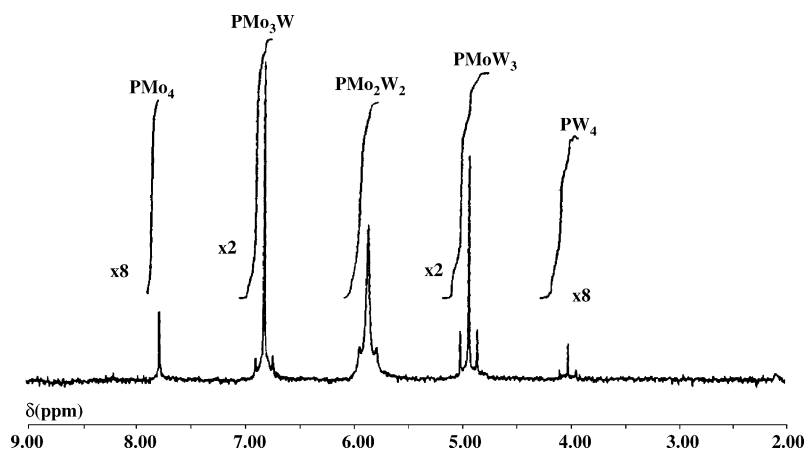
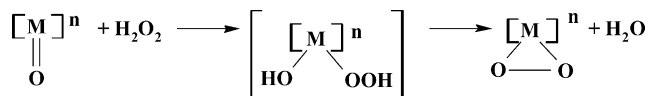


Fig. 9. ^{31}P NMR spectrum of a 1/1 mixture of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{PMo}_4\text{O}_{24}]$ and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{PW}_4\text{O}_{24}]$ in acetonitrile- d_3 . The spectrum was recorded immediately after preparation of the solution ($T \approx 297\text{ K}$), see ref. [17,18,29].

to the equilibrium between tridentate anions $\mu_2\text{-}\eta^2\text{:}\eta^1\text{-O}_2^{2-}$ and bidentate $\eta^2\text{-O}_2^{2-}$ for the peroxy groups of the $\{\text{M}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$ fragments [18]. This makes it difficult to identify the kinetically active species, since there is also fast equilibrium with all the “PW_x” anions ($x=1\text{--}4$); once more, the isolable species are often not those that lie along the principal reaction coordinates for catalysis [17,18,29].

7. Oxoperoxo species for the molecular design of supported oxidation catalysts and to avoid generation of polyoxometalates (two- or three-phase systems)

Ordinary silanols such as triphenylsilanol, Ph_3SiOH , diphenylsilanediol, $\text{Ph}_2\text{Si}(\text{OH})_2$, and 1,1,3,3-tetraphenyldisiloxane-1,3-diol, $[\{\text{Ph}_2\text{Si}(\text{OH})\}_2\text{O}]$, can be employed for the modelling of monopodal or dipodal surface attachment of metal ligand fragments corresponding to isolated surface hydroxyl groups such as lone or free, vicinal and geminal silanols (Fig. 7) [56,61]. The isolation of these mono- or dimeric oxoperoxo complexes led us to think that $[\text{MO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$ and even $[\{\text{Mo}(\text{O}_2)_2(\text{H}_2\text{O})\}_2(\mu\text{-O})]$ are more advantageous than $\text{Na}_2[\text{MoO}_4]$, $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]$, $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6[\alpha\text{-H}_2\text{W}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$, etc. currently used to prepare supported molybdenum (or tungsten) catalysts with silica, alumina or silica-alumina. This proposed route relies upon several observations. (i) From studies on systems of aqueous $[\text{MO}_4]^{2-}$ and $[\text{Mo}_7\text{O}_{24}]^{6-}$ solutions and silica, it is known that Mo(VI) (and even W(VI)) uptake by SiO_2 is relatively low over the entire pH range, except for a small increase at $\text{pH} \approx 2$ or lower owing to the formation of $[\text{SiM}_{12}\text{O}_{40}]^{4-}$ ions, which commonly desorb into solution). (ii) On the other hand, silica and molybdenum (or tungsten) low-nuclearity oxoperoxo species interact in aqueous acidic media to form fairly stable surface peroxy species; even if the peroxy ligands are unstable and decompose during thermal treatment to give oxo groups, they will be potential sites which can be regenerated as surface complexes according to a well-known process:

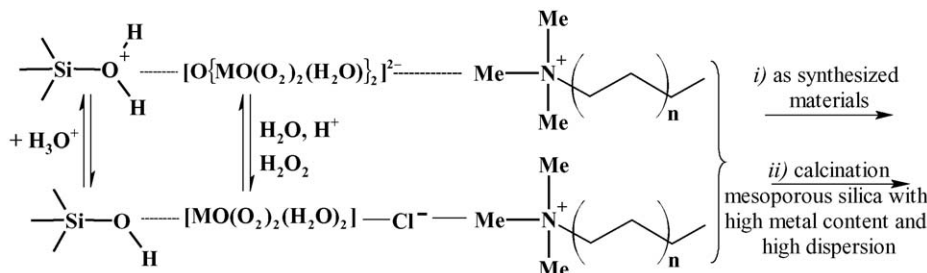


(iii) The target processes have been considered (economic factors, attrition strength ...). An original approach for incorporating molybdenum, tungsten or rhenium species, first into a mesostructured silica matrix, using low-nuclearity peroxi-

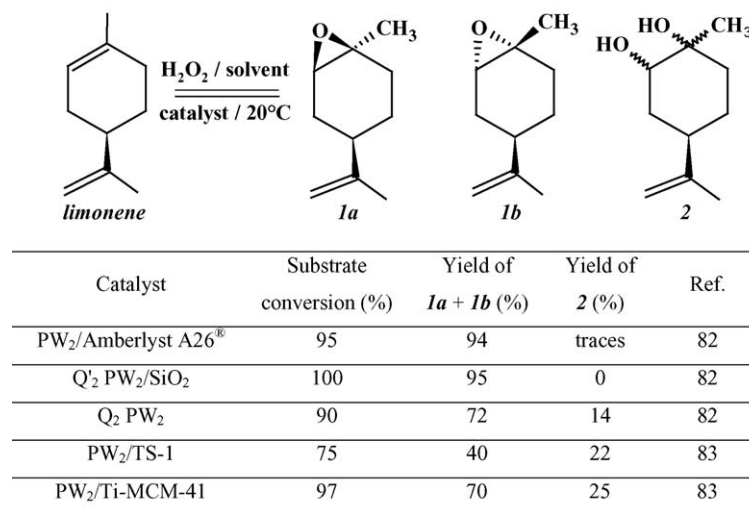
dic species in acidic medium was proposed (Scheme 3). This methodology was developed first for MoO_x -containing MCM-41 [75] and has been successfully extended to WO_x - or ReO_x -MCM-41 [76–78] and MoO_x -SBA-15 [79]. Several physicochemical techniques (powder X-ray diffraction, Raman spectrometry, ^{29}Si NMR, IR and UV spectrometry, EDX, elemental analysis) show that high incorporation levels (Si/M molar ratio of the order of 35/1) can be obtained, with a nearly homogeneous distribution of the dopants after heat treatment. In contrast, without an oxoperoxo metal precursor (polyoxo route), there is generation of polyoxometalates [80], which lead to phase segregation of the calcined materials: formation of MO_3 clusters or of oligomeric amorphous surface species, depending on to the thermal treatment. The very dispersive structure of the MO_x /siliceous mesoporous materials promotes the generation of highly active oxidation catalysts, but initial leaching of the redox-active species by nucleophilic reagents (*t*-BuOOH, $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, etc.) was observed. It appeared that thermal treatment can decisively modify the resistance to attrition and to leaching (less than 2 ppm [81]). Are the catalytic performances of mesoporous materials superior to those of analogues obtained by transposition or prepared conventionally? The methodology developed for the insertion of MoO_x into mesoporous materials (MCM-41 and SBA-15) has been successfully extended to the preparation of MoO_x on precipitated silica by wet impregnation [81].

The ease and the low cost of their synthesis, as compared to mesoporous catalysts, make them good candidates not only for oxidation reactions but also for other uses of molybdenum(VI)–silica catalysts [81]. To the best of our knowledge, $\text{SiO}_2/\text{MoO}_3$ binary condensed-phase diagrams are not known. The so-called “peroxy-route” with low-nuclearity peroxy metal precursors appears as an elegant method for combining these two oxides, which have, a priori, no strong affinity, and to obtain fair molybdenum (or tungsten) content and high dispersity.

For tungsten(VI) oxoperoxo-catalysed epoxidation with H_2O_2 , one may use supported $[\text{HPO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]^{2-}$ on resins or silica [82]. Amberlyst A26[®] was the macroreticular resin used. The “PW₂” complex (onium salts) was also supported onto dehydrated porous silica. The catalysts were found to be highly selective for the epoxidation of limonene by aqueous H_2O_2 at room temperature (Scheme 4). The $[\text{HPW}_2\text{O}_{14}]^{2-}$ anion can be trapped by the $\equiv\text{Si-OH}_2^+$ species, thus favouring ring-opening of epoxide to form 1,2-diols.



Scheme 3. Proposed intermediates in the synthesis of mesoporous materials incorporating $\text{M} = \text{Mo}$ or W .



Scheme 4. Epoxidation of limonene with supported “PW₂” species at RT. PW₂: [HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}]²⁻; Q' = (*n*-Bu₄N); QCl = Arquad 2HT[®]; Amberlyst A26[®] is a macroreticular resin.

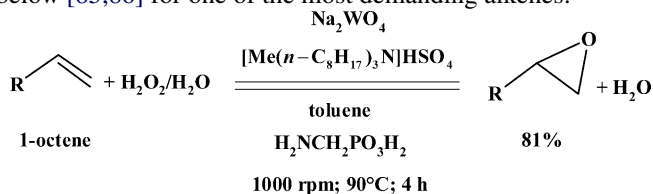
Stable associations with E compounds (E = P(V), As(V), S(VI), Si(IV), etc.) of oxoperoxotungsten species such as [HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}]²⁻ have been anchored on the external surface of titanium silicate (TS-1) or on Ti-MCM-41 which provide docking points, Ti(IV), to bind “PW₂”. The resulting supported catalysts, with 30% H₂O₂, are capable of converting limonene at RT mainly to 1,2-epoxides (Scheme 4). This is a clear demonstration that oxoperoxo tungsten(VI) is the active species, since limonene is too large to reach the titanium(IV) sites in the TS-1 micropores, and the Ti centres of the external surface cannot activate H₂O₂ under these conditions. (anchoring was controlled by ESCA and ³¹P NMR) [83].

Phosphate species modify the TS-1 or Ti(IV)-MCM-41 surface and can be used to anchor oxoperoxotungstate species. The “PW₂” species interact more strongly with Ti(IV) centres than with silica. Apart from its intrinsic interest, we think that this may have some chemical significance as a possible model for preparing catalysts.

Alternatively, as the phosphoramidate moiety has been tethered to the inner surface of MCM-41; the -NH-PO₃H₂ group binds the W-oxoperoxo complex with the formation of P-O-W bonds. It has been claimed that the resulting catalysts are heterogeneous [84].

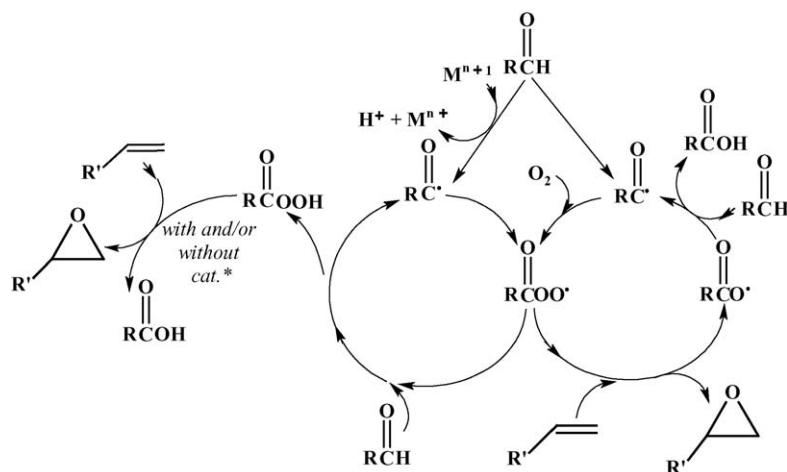
Following the research on “PW_n” and on rhenium(VII)-oxoperoxo based systems, that were at first sight solvolytically stable, to aqueous hydrogen peroxide, many variants have been derived; the data are growing impressively and will be the subject of a more extensive review. We just comment on some of the new proposals.

Among them, the Noyori et al. method which is presented below [85,86] for one of the most demanding alkenes:



Although epoxidation is considered to proceed via oxoperoxotungsten complexes under entirely halide-free conditions, the mechanistic details are unknown (existence of two assembling ligands or more), and difficult to determine at 90 °C. Note that (i) The (aminomethyl)phosphonic acid decomposes under the reaction conditions to form mainly H₃PO₄ and/or [HPO₄]²⁻. (ii) The P(V):W(VI) ratio corresponds to that for the synthesis of [HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}]²⁻, and there is a “deficiency” of Q⁺ (Q⁺ : P(V) ≈ 0.5 instead of 2 for “PW₂”), a result which compare favourably with other “optimization studies” [39,82,87,88]. (iii) The phase-transfer catalyst which is synthesized from (C₈H₁₇)₃N and toxic dimethyl sulfate is not easily available. (iv) Safety risks on a larger scale have to be evaluated. This modified system is useful for preparing adipic acid from cyclohexene, which is obtained by selective hydrogenation of benzene only in Japan (Asahi Chemical Industries). Dawson-type heteropolyoxometalate [R₄N]₄[S₂W₁₈O₆₂]/CH₃CN/H₂O₂-H₂O systems have also been used to prepare adipic acid in high yield [89]. The active species, maybe [SO₄{W₂O₂(μ-O₂)₂(O₂)₂}]²⁻, etc. have not been identified. Many groups revisited the necessary and time-consuming optimization with PW_n complexes. Recycling by means of proposed “Green Chemistry” systems remains a controversial subject; for example, it was found that ionic liquids are more toxic for the aquatic environment than methanol, dichloromethane, acetonitrile, etc. [90]; they cannot be used with aqueous hydrogen peroxide and/or dioxygen.

It has been found that PMo₄ species are minor complexes in the thoroughly studied *bleach media* and that a “OMo(diperoxo)P(V)” complex seems to be the only oxoperoxomolybdophosphate species of importance. Again, from dynamic studies it can be concluded that the species identified are in chemical exchange and that there is no direct chemical exchange between free [PO₄]³⁻ and “Mo₂X₄P” complex where X is [O₂]²⁻. Provided that molybdate can be recycled, oxoperoxomolybdate chemistry in a sodium sulfate medium can be used to obtain a selective and effective *non-chlorine process* suitable



Scheme 5. Reaction mechanism in alkene epoxidation by dioxygen in the presence of an aldehyde [37,94] catalysed by cat* = inorganic complexes or POMs.

for a closed pulp system—since Na⁺ and [SO₄]²⁻ are among the most common ions present in industrial bleach industry [91].

The “PW₂” [22] species as well as “AsW₂” [51] can compete with “AsW₄” [38] or “PW₄” [11] for converting olefins (propene and higher olefins) to epoxides using aqueous H₂O₂ in a liquid two-phase reaction system. The oxidation is claimed to be catalysed by a compound consisting of a phosphate-stabilized peroxotungstate species having a W:P atomic ratio of 2:1 [92]. For recent studies devoted to sophisticated systems for the synthesis of propylene oxide (PO) with H₂O₂, catalysed by “PW_n”, see [93].

8. A dream and/or a serious challenge: why not dioxygen?

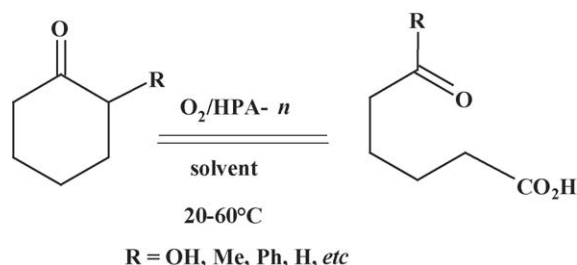
Despite the advantage of the use of air or dioxygen as the oxidant, there are relatively few methods known that use homogeneous catalysts or inorganic materials *under very mild conditions* for highly selective oxidations.

Monooxygenase-like systems: “aldehyde (coreducer)/dioxygen/solvent/alkene” systems for epoxidation at room temperature, can be catalysed by sophisticated complexes as well as by mononuclear inorganic complexes and even inorganic oxides and POMs [37,94]. There is evidence for percarboxylic acid formation in the reaction medium which, by itself, and/or with the formation of “[M]=O” complexes, can promote the epoxidation of the olefinic substrate (Scheme 5).

Parent systems for the epoxidation of propylene with dioxygen in primary alcohol (methanol, etc.) and secondary alcohol (*i*-propanol) over an oxoperoxoheteropoly compound “PW₂” immobilized on palladium-exchanged HMS were proposed [95]. The simultaneous existence of Pd and “PW₂” in the solid catalyst is claimed to be very important for improving the yield of propylene oxide (PO). Hydroperoxo species, –Pd–OOH [96] and/or H₂O₂, generated from the alcoholic solvent would regenerate the “PW₂” peroxo species. Analogues are studied by many groups and will be reviewed elsewhere; depending on the coreducers (dihydrogen, methanol, *i*-propanol, etc.) the catalysts and

the design of the reactor, a great number of combinations can be proposed. Another challenge would be the creation of true dioxygenase-like systems.

These examples are given to demonstrate the oxidative properties of transition-metal-substituted polyoxometalates such as “H₅[PMo_{12-n}V_nO₄₀].aq” (see Section 5). This catalyst has been extensively investigated [2,17] for the oxidative cleavage of cyclic ketones [68,97,98,99], of vicinal diols [100], and of α-ketols [99,101] in the presence of dioxygen under very mild conditions. For example, 2-hydroxycyclohexanone is oxidatively cleaved at 60 °C and even at room temperature in the presence of dioxygen to form adipic acid [99,101,102] with 100% selectivity at 90–97% conversion, according to Scheme 6. The oxidative cleavage of 1,2-cyclohexane-diol occurs at 75 °C in ethanol (or methanol) and oxygen atmosphere, and adipic acid diester is obtained with 90% selectivity at 62% conversion [100]. These oxidative systems can be considered as models of *dioxygenases* [17,68,97,102]. The reactions are of practical interest and were traditionally achieved using stoichiometric oxidants such as periodates or lead tetraacetate causing the already-mentioned pollution problems which can be avoided by these HPA catalysts as well as by simple precursors [17,102–105]. The catalytic behaviour of such oxidation catalysts might be promising for oxidative cleavage. Because of their high reactivity and structural flexibility, catalysts based on heteropoly compounds are of considerable interest and are potentially quite promising for the



Scheme 6. Catalytic reactions with “atom economy” and high selectivity.

synthesis of intermediates and fine chemicals [17,101]. Compared to most existing systems for C–C bond cleavage, the HPA-*n* systems require no organic solvent (water can be used) and have a broad scope in organic synthesis [17,98,99].

Nafion®-supported vanadium catalysts based on the [VO₂]⁺/[VO]²⁺ couple [105] or on modified HPA-*n* species are fairly active for cyclohexane oxidation: they give oxygenated products (aldehyde or keto acids, α, ω-diacids, alcohols, ketones, lactones). High yields and conversions have been obtained [17]; thus they compete with the recently proposed gold-based systems? In each case optimization studies must be performed with complete mass balance for the gold cluster/dioxygen systems [106]. At present dioxygenase-like systems already exist with HPA-*n*/O₂ and 2-hydroxycyclohexanone and several α-substituted cyclohexanones [17].

9. Conclusion

The success stories of the TiO_x-on-SiO₂ catalyst, invented at Shell in 1970, and the famous titanium(IV) silicalite (TS-1) from Enichem, whose catalytic activities are attributed to site isolation of Ti(IV) [107], preventing the formation of inactive oligomeric surface species, have contributed to a rational approach for the design of solid oxidation catalysts. Reinvestigations of molybdenum- and tungsten-based precursors, particularly of Keggin heteropolyanions and of rhenium(VII) complexes, such as [(CH₃)ReO₃], all in the presence of hydrogen peroxide have opened up new possibilities based on unsuspected species for the development of homogeneous, two-phase (with or without phase-transfer agent) and even heterogeneous systems. We think that highly effective solid catalysts for mild oxidations should be developed in the next future, keeping in mind that the perfect catalyst does not exist (both TS-1 and TiO_x-on-SiO₂ release unexpectedly Ti(IV) in liquid phase processes—and even Si(IV), in our hands!). Nevertheless, inorganic catalysts or precursors, without any oxidizable ligand, easy to prepare and to apply, are the trump card for oxidation catalysis under very mild conditions. The development of mesoporous materials and of methodologies for the insertion of MO_x (M = Mo, W, Re, etc.) into these materials are in progress. Once again, the use of low-nuclearity oxoperoxo species should be considered for the preparation of catalysts with site isolation of Mo(VI), W(VI) or V(V): the so-called “peroxo route”, is an elegant method for combining oxides such as MO₃ (M = Mo or W) and SiO₂ which have a priori no strong affinity, and to obtain fair metal content, high dispersity and fully recyclable catalysts.

Recent developments for the activation of dioxygen and highly selective dioxygenase-like catalytic reactions, based on polyoxometalates or on low-nuclearity species, are also very promising, as shown for α-substituted cycloalkanones in liquid phase. We have shown that the reactivity of precursor complexes, even if kinetic data are not easily obtained (cf. fluxionality, exchange of building blocks, etc.) leads to a more rational approach to catalysis systems and to the discovery of novel classes of precursors and/or catalysts.

Note added in proof

Shiro Ikegami's group works on a self-assembling temperature-responsive polymer with a quaternary ammonium unit. The counter-ion, [PW₁₂O₄₀]³⁻ is the pre-catalyst for the desired reaction: the oxidation of alcohols by hydrogen peroxide (10%). The catalyst forms a stable emulsion in water with high catalytic activity (at 90 °C). The polymer precipitates as it cools and can easily be separated. This switchable catalyst does involve POMs to POPOMs and back again. Comparison with supported [HPO₄{W₂O₂(μ-O₂)₂(O₂)₂}]²⁻ on resins or silica [82] operating at room temperature would be of interest. See: H. Hamamoto, Y. Suzuki, Y.M.A. Yamada, H. Takahashi, S. Ikegami, *Angew. Chem. Int. Ed.* 44 (2005) 4536–4538. A recyclable catalytic system based on a temperature-responsive catalyst.

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