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Homogeneous catalysis by transition metal oxygen anion clusters

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Contents

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Abstract

This review provides a thorough discussion of homogeneous catalysis by transition metal oxygen anion clusters (polyoxometalates), with a focus on mechanism. The primary catalysts examined are mixed addenda and d-electron-transition-metal-substituted polyoxometalate (TMSP) complexes. The unusual versatility and tunability of these catalysts and their compatibility with environmentally and economically attractive conditions (solvents, oxidants, etc.) are outlined. A general compilation of the reactions, including catalytic electrooxidations or electroreductions, reported to date is given. Selected examples involving different classes of catalysts, different organic substrates and transformations, and mechanistic information are covered.

Keywords: Homogeneous catalysis; Polyoxometalates; Redox chemistry; Addenda ions

1. Introduction

1.1. General considerations and literature

Homogeneous catalysis by early-transition-metal-oxygen-anion clusters, henceforth referred to as polyoxometalates or polyoxoanions for convenience, is a rapidly growing area, in part as a consequence of the unusual versatility of these catalysts and their compatibility with environmentally friendly conditions (e.g. O_2 and H_2O_2) and operation. This initial overview section is followed by sections that focus on the general properties of polyoxometalates, the pertinent redox chemistry, and finally, the homogeneous catalysis itself. This review focuses on the detailed features, including the mechanisms, of the catalytic processes for two reasons. First, previous reviews have not covered this fundamental chemistry very adequately, and second, a deep understanding of just this fundamental chemistry will be requisite for more sophisticated applications and developments in this area, including catalysts for transformation of a range of complex targets in biology, chemistry and materials science. Reasonable projected tasks entail recognition and transformation of complex multifunctional molecules and asymmetric catalytic reactions. The unique collective properties of polyoxometalates make them of fundamental and practical interest. There are already more commercial applications of polyoxometalates than for any class of cluster compound and the promise for additional applications in areas from catalysis and medicine to materials and microdevice technology is substantial. There have been more than thirty reviews on some aspect of polyoxometalates since 1983 [1–31]. Most of these reviews, including ones by Day and Klemperer, [3] Chen and Zubieta, [2] Isobe, [12] and Pope [28], stress structural properties. One by Jeannin addresses nomenclature [14] and others by Papaconstantinou [25], Yamase [31] and Hill and McCartha [10] address photochemistry and photocatalysis. While many photocatalytic processes are very similar to those described in Section 3 of this review, this work has not been formally included here as it has recently been reviewed elsewhere [10]. It has been more than seven years since the last fairly comprehensive and general reviews of polyoxometalates [26,27] and the enormous growth in the chemistry of these compounds makes such reviews increasingly difficult and impractical. An excellent general review by Pope and Müller appeared 4 years ago but was prohibited by space limitations from delving into much detail [29]. A 411-page edited volume from the polyoxometalate meeting in Bielefeld held during the summer of 1992 compiles a series of 28 articles focusing on a range of subtopics. While some of the included articles provide fairly up-to-date reviews, others are simply research reports of the most recent findings in specific research areas [29].

In addition, there are several reviews on one or more aspects of catalysis by polyoxometalates. Effective processes involving both heterogeneous and homogeneous catalysis by polyoxometalates are well documented and good reviews covering the commercialized processes have been written recently by Misono [20,21]. The first review on catalysis, written by Matveev and Kozhevnikov, thoroughly discussed aspects of heteropolyacid catalysis with an emphasis on homogeneous oxidative and acid processes. Physicochemical properties of the complexes, mechanism, and applications were addressed [17,18]. Kozhevnikov followed with two reviews in 1987 and 1993 which concentrated on the advances in homogeneous and heterogeneous catalysis by heteropolyacids; and their application as acid and oxidation catalysts for the synthesis of fine chemicals, including antioxidants, medicines and vitamins [15,16]. Hill discussed polyoxometalates as catalysts for selective catalytic homogeneous oxygenation [8,9]. Ono surveyed the use of heteropolyacids as oxidation and acid catalysts [24]. Mizuno and Misono reviewed recent progress in both homogeneous and heterogeneous catalysis by heteropolyanions [20,22,23] and Jansen et al. reviewed the same subject with an emphasis on the last 6 years of research [13]. The subject matter in several of the latter reviews is repetitive. All these reviews are more descriptive than quantitative. There is little rigorous discussion about how these reactions actually take place. Indeed, hard mechanistic information on polyoxometalate-catalyzed reactions is limited to a handful of papers. This review tries to remedy this deficit and concentrates primarily on the most recent research (roughly the last 4 years of work). Discussion of studies prior to this can be found in the appropriate reviews cited above.

Much work has been done in the area of H_2O_2 oxidation catalyzed by heteropolyacids and two reviews focused on this work. One review by Ishii and Ogawa focused on hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridium chloride [11]. A wide selection of organic substrates and reactions were addressed, including epoxidation, oxidative dehydrogenation and oxidative cleavage processes, but very little information was offered about how the reactions actually take place. Another review by Hill addressed H_2O_2 facilitated by polyoxometalates [6]. While these two reviews are relatively recent, both are already quite out of date as research in this area, and in particular that involving polyperoxotungstophosphates and their oxidation chemistry, has developed considerably in the last 3 years [32–40]. Most of the recent general reviews of polyoxometalate catalysis include oxidations by H_2O_2 and the precatalysts, $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$, and other polyoxometalates, but inclusion of these reactions in such reviews is questionable given that lower nuclearity polyperoxometalates are the dominant and active species formed in these systems [33–41]. Recent data provide strong evidence that the polyoxometalate catalyst precursors are not catalytically significant [33,35,36]. The polyperoxometalates are very different structurally and electronically from the polyoxometalate precursors. Primarily for these reasons and secondarily as these systems no longer appear to be of serious commercial value given the requirement of chlorocarbon solvents or selectivity issues [42,43], they will not be discussed further. Brégeault and co-workers [35] and Hill and co-workers [36] have investigated the mechanisms of epoxidation under Venturello's conditions (H^+, WO_4^{2-}, PO_4^{3-}, phase transfer catalyst, $H_2O/CHCl_3$, 60 °C) and under Ishii's conditions ($H_3PW_{12}O_{40}$, phase transfer catalyst, $H_2O/CHCl_3$, 60 °C). Amusingly, these studies indicate that these catalytic systems are effectively identical despite the fact that each group patented their particular set of catalyst precursors as novel chemistry [44,45]. In closing this section, we note that a thorough review of dioxygen and peroxo complexes with a focus on structural features has just appeared [4].

Heterogeneous reactions catalyzed by polyoxometalates have been repeatedly reviewed and few major strides regarding the nature of these reactions have been made recently [13,19–24]. As a consequence, yet another review of this material, at least with the conventional technical foci, would contribute little. Misono's multiple reaction domains, "pseudoliquid phase" and other concepts in heterogeneous catalysis by polyoxometalates were nicely elaborated years ago [19,21]. Acid catalysis by polyoxometalates is not a primary focus of this review as the nature and mechanism of these reactions is likely to be similar to the same reactions catalyzed by other strong Brønsted acids. One of the most promising applications of polyoxometalates in catalysis is as insoluble superacids and this research was reviewed recently by Misono [46]. As a majority of the catalytic reactions we will review are oxidations, we follow the next section on basic features of polyoxometalates with a section on basic features of metal catalyzed oxidations including mechanisms.

1.2. *Polyoxometalates*

This section has been kept to a minimum as this material has been covered not only in all the general reviews but also in abbreviated form in the catalysis reviews. Polyoxometalates are a large and rapidly growing class of compounds. They are constituted, as the name indicates, primarily by d^0 early transition metal cations and oxide anions. The principal d^0 transition metal ions that form the molecular structural framework or scaffolding of polyoxometalates are W(VI), Mo(VI), V(V), Nb(V), Ta(V) and Ti(IV). These ions or their local MO_x coordination polyhedra are referred to as "addenda" or "addenda ions". There are two generic families of polyoxometalates, the isopolyoxometalates or isopolyanions, which contain only transition metal cations and oxide anions, and the heteropolyoxometalates or heteropolyanions which contain one or more p or d block elements as "heteroatoms" located at structurally well defined sites, in addition to the more numerous transition metal and oxide ions. As the suffix of polyoxometalates indicates, these compounds are nearly always negatively charged although the negative charge density is widely variable depending on the elemental composition and the molecular structure.

1.2.1. Structure

Polyoxometalates are composed primarily of MO_6 octahedra but in some cases by MO_5 pentahedra and MO_4 tetrahedra. The most commonly occurring MO_6 octahedra are those containing one terminal oxo group and five bridging oxo groups (Type I octahedra) and those containing two terminal oxo groups and four bridging oxo groups (Type II octahedra) [26]. The three-dimensional structures of polyoxometalates are defined primarily by corner sharing (one bridging μ_2-oxo group), edge sharing (two bridging μ_2-oxo groups), or occasionally by face sharing (three bridging μ_2-oxo groups) MO_6 octahedra. While there is a profound structural diversity in polyoxometalates, a diversity that has been markedly enhanced by an avalanche of new complexes characterized by X-ray crystallography in the last 5 years, a few structures still dominate polyoxometalate research in many areas. The most investigated of all structural types are the Keggin heteropolyanions of formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$, when $M=W(VI)$ or Mo(VI). The heteroatom, X^{n+}, can be one of over half the d block elements and many of the p block elements. These complexes are attractive as they are very stable, readily prepared and well characterized spectroscopically. They also exhibit a rich and well elaborated substitution chemistry in which one or more of the d^0 addenda W(VI) or Mo(VI) ions can be replaced with other d^0 early transition metal (addenda) ions, d-electron transition metal ions, or organometallic or organic groups. Fig. 1 illustrates in atom ("ball-and-stick") notation five representative polyoxometalate structures. Fig. 2 illustrates in polyhedral notation four representative heteropolyanion complexes that feature prominently in this review on homogeneous catalysis. In polyhedral notation, the MO_x polyhedra are depicted; the nuclei of the oxygen atoms are the vertices and the metal ions are buried inside each polyhedron. The inter-MO_x connections (e.g. corner sharing versus edge sharing) and longer range structural features are often more readily discerned in polyhedral notation than in bond notation.

1.2.2. Reactivity

Solubility, a requisite for homogeneous catalysis, is quite controllable for polyoxometalates as these complexes can be dissolved in media from water to hydrocarbons by judicious choice of the counter cation(s). The redox characteristics of the polyoxometalates which are important for certain types of homogeneous catalysis are also widely variable and to some extent controllable. One early criterion for redox chemistry attributable to Michael Pope was that polyoxometalates composed of Type I MO_6 octahedra display reversible redox chemistry while polyoxometalates composed of Type II MO_6 octahedra do not, a criterion that follows from a simple MO picture of the two types of MO_6 units [26]. The redox potentials depend, in part, on negative charge density and elemental composition. The negative charge density depends principally on structural type, protonation state and elemental composition, all of which can be controlled to a reasonable extent synthetically. The dependence of polyoxometalate redox potentials on elemental composition is dictated primarily by the presence or absence of the most oxidizing skeletal or "addenda" d^0 early transition metal ions. The polyoxometalate addenda ions in order of decreasing redox potentials are V(V) (most oxidizing)>Mo(VI)>W(VI) (least oxidizing).

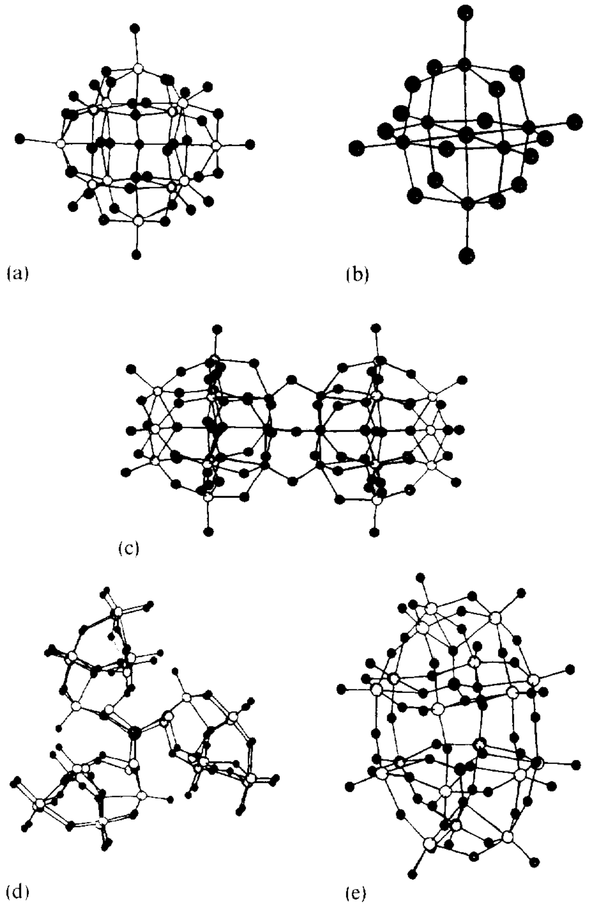


Fig. 1. Atom ("ball-and-stick") drawings of five representative polyoxometalate structures. (a) the Keggin structure, the most common polyoxometalate structure, of formula $X^{n+}M_{12}O_{40}^{(8-n)-}$, X^{n+} = over half the elements in the periodic table and M = Mo(VI) or W(VI); (b) the O_h-symmetry hexametalate structure, one of the simplest polyoxometalate structures, of formula $M_6O_{19}^{x-}$, M = V(V), Nb(V), or Ta(V) and $x = 8$ or M = Mo(VI), W(VI) and $x = 2$; (c) the C_{3v}-symmetry dimeric complex of formula $Si_2Nb_6W_{18}O_{77}^{8-}$; (d) the C_{3h}-symmetry HPA-23 structure of formula $[MSb_9W_{18}O_{86}]^{18-}$, M = Na(I), K(I), others; (e) the D_{3h}-symmetry Wells–Dawson structure of formula $\alpha\text{-}X_2M_{18}O_{62}^{y-}$, X = P(V), S(VI), As(V), M = Mo(VI), W(VI) and y varies accordingly.

There are no known examples involving reduction of Nb(V), Ta(V), or Ti(IV) ions in dissolved polyoxometalates.

One polyoxoanion counter cation, H^+, has relevance for homogeneous catalysis and catalysis by polyoxometalates in general. The proton or the free acid forms of polyoxometalates are stable, tractable and highly soluble for several structural classes of polyoxometalates. In addition, the free acid forms become superacids when dehydrated, and as such they can function as effective and recoverable catalysts for a variety of acid-dependent processes [46]. The simultaneous exhibition of the above

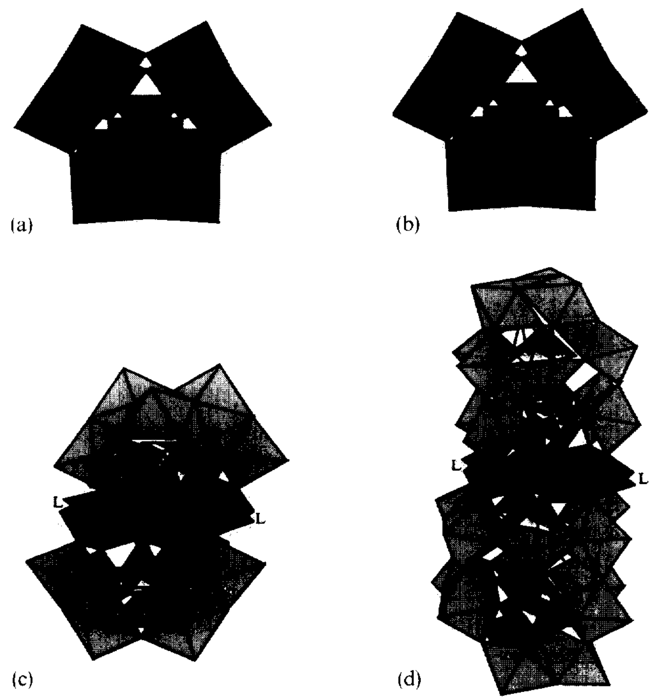


Fig. 2. Polyhedral drawings of four structural families of polyoxometalates used extensively to date in homogeneous catalytic oxidation research. (a) the parent Keggin structure; (b) a mono-substituted Keggin derived "transition-metal-substituted polyoxometalate" or TMSP complex; (c) the trivacant Keggin sandwich (TKS) complexes of formula $M_4(PW_9O_{34})_2^{10-}$, M = Co(II), Zn(II), Cu(II), Mn(II) and Fe(III/II); and (d) the trivacant Wells–Dawson sandwich (TWDS) complexes of formula $M_4(P_2W_{15}O_{56})^{16-}$, M = Co(II), Cu(II), Mn(II), Fe(III/II), etc. For both the TKS and TWDS complexes, the 4 ions in the middle can be varied to a considerable extent. See text for explanations of polyhedral notation, acronyms and other points.

and other properties has rendered polyoxometalates attractive in homogenous catalysis and a range of areas.

1.3. Homogeneous catalytic oxidation

1.3.1. General considerations

As a sizable majority of the research in homogeneous catalysis by polyoxometalates involves oxidation processes, it is necessary to outline the fundamental features of homogeneous catalytic oxidation. Research in this area has been quite intense in the last few years for several reasons: (1) catalytic oxidations are often the most challenging to achieve satisfactorily (high yields and selectivities, etc.), (2) the existing catalytic processes often leave considerable room for improvement, (3) the mechanisms are often quite complex (e.g. multiple mechanisms can be simultaneously operable), and (4) these processes have extensive application in areas from the manufacture of fine chemicals to the degradation of many kinds of toxic materials. Several reviews and symposia in this area have recently been published [7,47–56]. The generic catalytic oxidation process is given in Eq. (1) and a general catalytic oxo transfer oxidation (or oxygenation) process, a major subset of Eq. (1), is given in Eq. (2).

$$\mathrm{Sub} + \mathrm{OX} \xrightarrow[\text{(catalyst)}]{\mathrm{L_nM}} (\mathrm{Sub})_{\mathrm{ox}} + \mathrm{RED} \tag{1}$$

$$\mathrm{Sub} + \mathrm{DO} \xrightarrow[\text{(catalyst)}]{\mathrm{L_nM}} \mathrm{SubO} + \mathrm{D} \tag{2}$$

where Sub = organic substrate, OX = oxidant, DO = oxygen donor.

1.3.2. Oxidants

A large number of oxidants, OX in Eq. 1, many of which can function as oxygen donors, DO in Eq. (2), have been extensively investigated in context with homogeneous catalytic oxidation processes. The primary characteristics that define the attractiveness of an oxidant are the % active oxygen (the higher the better) and the selectivity associated with its use, in addition to the pragmatic issues of cost and effect on the environment. Some of the major oxidants, particularly those with oxygen atom donor capabilities, along with salient assets and liabilities are summarized in Table 1. Table 1 is organized from the highest % active oxygen at the top of the table to the lowest % active oxygen.

While the oxidants such as OCl^-, Cl_2 and ClO_2 lead in varying yields to chlorinated organic compounds, including the highly toxic and carcinogenic dioxins and are, as a consequence, rapidly becoming environmentally unacceptable, many other oxidants that produce only minimally toxic inorganic waste as by-products, such as sulfate from persulfate, are also becoming environmentally and hence politically and economically unacceptable. Indeed, legislation in many countries concerning the waste products from industrial catalytic oxidation processes is moving so fast it has been difficult for companies developing new and more benign catalytic processes to keep up. Some better processes from the environmental prospective are obsolete before sufficient development is concluded to render them commercially viable. The most attractive oxidants with respect to the criteria articulated above are O_2 and H_2O_2. Unfortunately, these two oxidants generally exhibit the most complex and minimally controllable oxidation chemistry of all the potentially attractive oxidants.

1.3.3. General mechanisms

Fig. 3 (Eqs. (3–11)) summarizes the general processes in homogeneous metal-catalyzed oxidation processes. Radical chain processes, including those associated with O_2 (autoxidation) and H_2O_2, that entail a minimal involvement of the metal are not included here. Oxo transfer, Eq. (3) in Fig. 3, is clearly important if not dominant in the most difficult enzymatic oxidations and the oxidation reactivity of high-valent transition oxometal species is among the most variable and, in principal, electronically controllable. While a multitude of biomimetic systems using a range of oxygen donors (see Table 1) facilitate the oxygenation cycle of Eqs. (3) and (4)

Table 1
Major oxygen donor oxidants, DO

DO[a]	% Active oxygen	By-product (D)	Comments
O_2	100	None[b]	A commercially successful nonradical-chain system does not currently exist.
H_2O_2	47	H_2O	Attractive environmentally.
N_2O	36.4	N_2	Fairly attractive, minimally used, and inexpensive oxidant. Usually kinetically unreactive. May become more expensive soon.
O_3	33.3	O_2	Potentially environmentally attractive. Short lived and hard to store, corrosive.
ClO_2	23.9	ClO^-, Cl^-	Inorganic salt by-products. Toxic and carcinogenic chlorinated by-products.
ClO^-	21.6	Cl^-	Same as for ClO_2.
$(CH_3)_2CO_2$	21.6	$(CH_3)_2CO$	Highly reactive with metal.
t-BuOOH (TBHP)	17.8	t-BuOH	Still commercially important.
$C_5H_{11}NO_2$[c]	13.7	$C_5H_{11}NO$	Expensive, but the oxidant of choice (MMNO) in some catalytic oxidations.
ClO_3^-	13.1	ClO_2^-, Cl^-	Inorganic salt and chlorinated organic by-products.
HSO_5^-	10.5	HSO_4^-	Undesirable inorganic salt product.
$ClC_6H_4CO_3H$ (MCPBA)	10.2	$ClC_6H_4CO_2H$	Fairly expensive.
$NCC_6H_4N(CH_3)_2O$	9.9	$NCC_6H_4N(CH_3)_2$	Fairly selective in metal catalyzed oxidations; expensive.
IO_4^-	7.5	IO_3^-	Undesirable inorganic salt product.
C_6H_5IO (PhIO)	7.3	C_6H_5I	Often quite selective in metal catalyzed oxidations. Prohibitively expensive.
C_6F_5IO (PFIB)	5.2	C_6F_5I	Same as for C_6H_5IO.

[a] Common abbreviations are given in parenthesis after the oxygen donor. [b] No by-products should be observed provided reducing agent-free non-radical-chain aerobic oxygenation can be achieved. [c] *N*-methylmorpholine *N*-oxide.

(in Fig. 3), there are few commercially significant processes based on this mechanism thus far. The less reactive and alterable, but to date more selective and tractable oxo transfer reactions, involving heterolytic (non-radical) mechanisms and peroxometal intermediates (not shown in Fig. 3), are more commercially significant.

Reversible dioxygenation, Eq. (5) in Fig. 3, followed by reduction and peroxide cleavage to form high-valent oxoiron species (Eqs. (5) and (6) where M = Fe) are important in biological systems including the heme enzyme, cytochrome *P*-450 [57], and probably in the nonheme enzyme methane monooxygenase (MMO) [58–63]. Generation of the high-valent oxometal species via reaction of the dioxygenated metal complex, MO_2, with another equivalent of reduced metal complex, M, Eq. (7) in Fig. 3, is highly attractive as no external reducing agent is required. Only O_2 and

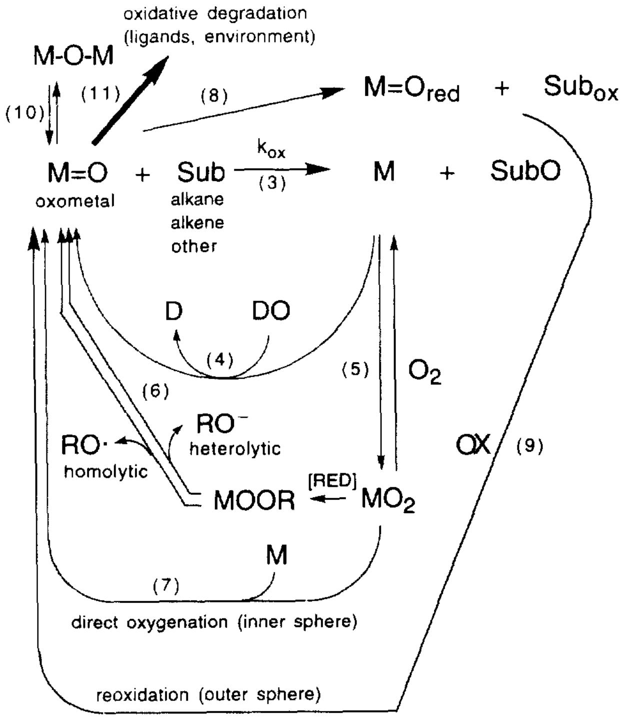


Fig. 3. General processes in homogeneous metal-catalyzed oxidation reactions. See text for explanation.

substrate are needed for the net catalytic cycle (Eqs. (3), (5) and (7), in Fig. 3). No commercially viable homogeneous catalytic oxidation based on this mechanism is available. Indeed, only two or three examples of this are known, with the best example being aerobic epoxidation catalyzed by tetramesitylporphyrinatoruthenium (II), Ru(II)TMP [64]. Unfortunately, the barriers to overcome before such a process were to be viable are collectively formidable. Homogeneous metal-based systems must be identified for which Eqs. (3), (5) and (7) all proceed in high yield and at satisfactory rates.

A final general mechanism for homogeneous metal-based oxidation is direct oxidation of substrate by the metal complex, Eq. (8) in Fig. 3, followed by regeneration of the reduced metal complex ($M=O_{red}$), Eq. (9) in Fig. 3, by the oxidant, OX. This process, Eqs. (8) and (9), is as inherently attractive as it is rare. One feature of considerable significance is that Eqs. (8) and (9) can be separated in either time or space. Such a separation facilitates the use of the most attractive oxidants such as O_2 and H_2O_2 without involvement of radical chain and other minimally selective and controllable oxidative processes often associated with their use. In closing the mechanistic overview of homogeneous metal-mediated oxidation processes, two side reactions, one nonproductive and one deleterious, should be mentioned. The nonproductive process involves μ-oxo dimer formation or dehydration condensations that are extensions thereof (Eq. (10) in Fig. 3). This process is often reversible, but not always so, under conditions where the catalytic oxidation proceeds satisfactorily (fast and selectively). The other process, oxidative degradation of the organic ligands or other necessary organic components, Eq. (11) in Fig. 3, is irreversible and is often the success-limiting factor with respect to development of viable homogeneous catalytic oxidation systems, particularly those that function on significant scales. Major efforts have been made by many research groups in recent years to combat this Achilles' heel of homogeneous oxidation catalysts, including construction of elegant but expensive polyhalogenated porphyrin and other organic ligand systems [48,51,56,65–79].

2. d-Electron-transition-metal-substituted polyoxometalate (TMSP) complexes

2.1. *Homogeneous catalytic reactions*

One or more addenda ions in some structural families of polyoxometalates can be substituted with d-electron transition metal ions. Syntheses of these d-electron-transition-metal-substituted polyoxometalates (TMSP) complexes date back to 1956 (substitution in Keggin heteropolyanions) [80]. Baker speculated in 1970 that "...the role of these complexes in catalysis should be important" [81]. Fourteen years later in breakthrough work, Katsoulis and Pope demonstrated that Keggin-type TMSP complexes, particularly $[(Mn^{II}H_2O)SiW_{11}O_{39}]^{6-}$, when extracted into nonpolar aprotic organic solvents, such as toluene, could reversibly bind O_2 [82]. These authors also speculated about catalysis, quoting: "Besides the obvious implications for catalysis and molecular activation, we foresee the development of novel high-temperature chemistry, new methods of synthesis and new polyanions and derivatives" [82]. The first actual catalysis (elaboration of specific concept and realization of successful results) came 2 years later (1986) in a communication by Hill and Brown [83]. The specific concept was oxygen transfer from a typical donor to a suitable TMSP followed by transfer of this TMSP-activated form of oxygen to an organic substrate (i.e. Eqs. (3) and (4) in Fig. 3). This work followed in a direct way from the thorough earlier investigations of analogous metalloporphyrin systems by the Hill group (catalytic profiles, characterization of intermediates, product distributions, kinetics and other studies in many papers) [75,84–92]. The realization was the sustained and selective oxygenation of alkenes by iodosylarenes catalyzed by $M^{II}PW_{11}O_{39}^{5-}$, $M = Co(II)$ or $Mn(II)$ (Eq. (12); numbers are % selectivities) [83]. Since this time, other TMSP complexes have been prepared, characterized and their catalytic chemistries evaluated with varying degrees of sophistication and thoroughness (Table 2). Again, the reactions given in Table 2 and discussed below are reactions reported primarily in the last 4 years. Table 2 excludes most articles discussed in reviews written prior to 1993.

Table 2
Reactions catalyzed by transition-metal-substituted polyoxometalate (TMSP) complexes

Catalyst[a]	Substrate	Solvent	Oxidant[b]	Products[c]	Comments	Reference
1. Monosubstituted TMSP catalysts						
$K_4CrPW_{11}O_{39}$	alkane	$H_2O/CH_3CO_2H/C_6H_5Cl$	O_2	not available	150 °C	[93]
$K_5(CrN_3)PW_{11}O_{39}$	alkane	$H_2O/Ch_3CO_2H/C_6H_5Cl$	O_2	alcohol, ketone	150 °C	[93]
$H_4FePW_{11}O_{39}$	alkane	CH_3CN	O_2	alcohol, ketone	150 °C	[70]
$K_4CrPMo_{11}O_{39}$	alkane	$H_2O/CH_3CO_2H/C_6H_5Cl$	O_2	alcohol, ketone	100 °C	[93]
$K_6MSiMo_{11}O_{39}$, M = Fe, Co or Mn	alkane	$H_2O/CH_3CO_2H/C_6H_5Cl$	O_2	alcohol, ketone	100 °C or 150 °C	[93]
$K_5(RuH_2O)PW_{11}O_{39}$	alkane	CH_2Cl_2/H_2O	NaClO or TBHP	alcohol, ketone	22 °C biphasic rxn	[94]
$^6Q_5MPW_{11}O_{39}$, M = Co, Mn, Cu or Fe	alkane	C_6H_6, $C_2H_4Cl_2$, or CH_3CN	TBHP	alcohol, ketone	65 °C argon	[95 98]
$^6Q_5MPW_{11}O_{39}$, M = Mn or Fe	alkane	C_6H_6	*m*CPBA	alcohol, ketone	24 °C argon	[97]
$^4Q_4HMPW_{11}O_{39}$, M = Mn or Co	alkane	CH_3CN	PhIO or PFIB	alcohol, ketone	25 °C argon	[97,99]
$^4Q_4HMPW_{11}O_{39}$, M = Fe or Cr	alkane	CH_3CN	PhIO or PFIB	no rxn	25 °C argon	[97,99]
$^4Q_4MnPW_{11}O_{39}$	alkane	Ch_3CN/CH_2Cl_2	PhIO	ketone, alcohol	20 °C argon	[100]
$^7Q_5(CrO)SiW_{11}O_{39}$	alkane	C_6H_6	$(Cr^V=O)$	ketone	50 °C argon	[101]
$^4Q_8(\alpha_2\text{-MnBr})P_2W_{17}O_{61}$	alkane	CH_3CN/CH_2Cl_2	PhIO	ketone, alcohol	20 °C argon	[100]
$^4Q_9(\alpha_2\text{-MBr})P_2W_{17}O_{61}$, M = Co, Ni, Cu	alkane	CH_3CN/CH_2Cl_2	PhIO	ketone, alcohol	20 °C argon	[100]
$^4Q_5MPW_{11}O_{39}$, M = Co, Mn, Cu, Ni or Fe	alkene	CH_3CN	O_2	epoxide allylic ketone allylic alcohol	303 K[d]	[102]
$^4Q_5CoPW_{11}O_{39}$	diene	CH_3CN or CH_2Cl_2	O_2 or PhIO	epoxide	303 K[e]	[103]
$^4Q_6(MnH_2O)SiW_{11}O_{39}$	alkene	C_6H_6	O_2	allylic ketone allylic alcohol	70 °C	[104]
$^4Q_6(MH_2O)SiW_{11}O_{39}$, M = Mn, Co or Fe	alkene	C_6H_6	O_2	epoxide allylic alcohol allylic ketone	70 °C $Na_2S_2O_4$[f]	[104]

$^4Q_6(CuH_2O)SiW_{11}O_{39}$	alkene	C_6H_6	O_2	no rxn	70 °C $Na_2S_2O_4$[f]	[104]
$^4Q_6(MnH_2O)SiW_{11}O_{39}$	alkene	C_6H_6	O_2	no rxn	70 °C ascorbate[g]	[104]
$^4Q_6(MnH_2O)SiW_{11}O_{39}$	alkene	C_6H_6	O_2	epoxide allylic alcohol allylic ketone	70 °C, H_2/Pt[h]	[104]
$^4Q_6(MH_2O)SiW_{11}O_{39}$, M = Co or Cu	alkene	C_6H_6	O_2	epoxide allylic alcohol allylic ketone	70 °C	[104]
$^4Q_6(FeH_2O)SiW_{11}O_{39}$	alkene	C_6H_6	O_2	no rxn	70 °C	[104]
$^4Q_6(MnH_2O)SiW_{11}O_{39}$	alkene	C_6H_6/CH_3Ch_2OH	O_2	alcohol allylic alcohol, alkane	70 °C, $NaBH_4$	[104]
$^4Q_6(CuH_2O)SiW_{11}O_{39}$	alkene	C_6H_6/Ch_3CH_2OH	O_2	alcohol	70 °C, $NaBH_4$	[104]
$^4Q_6(MH_2O)SiW_{11}O_{39}$, M = Fe or Co	alkene	C_6H_6/CH_3CH_2OH	O_2	no rxn	70 °C, $NaBH_4$	[104]
$^4Q_4FePW_{11}O_{39}$	alkene	CH_3CN	H_2O_2	epoxide allylic ketone	20 °C, argon	[7,105]
$^4Q_5FePW_{11}O_{39}$	alkene	CH_3CN	H_2O_2	epoxide allylic ketone	20 °C, argon	[106]
$^4Q_4HFePW_{11}O_{39}$	alkene	CH_3CN	H_2O_2	alcohol allylic ketone, diol	35 °C, argon	[107]
$^4Q_4CrPW_{11}O_{39}$	alkene	CH_3CN	H_2O_2	epoxide, alcohol allylic ketone, diol	35 °C, argon	[107]
$^6Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	$C_2H_4Cl_2$	TBHP	alcohol, ketone acid, aldehyde	60 °C	[108,109]
$^6Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	$H_2O/C_2H_4Cl_2$	$KHSO_5$	acid, aldehyde epoxide	60 °C	[108,109]
$^6Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	$H_2O/C_2H_4Cl_2$	$NaIO_4$	aldehyde, acid	60 °C	[108,109]
$^6Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	$C_2H_4Cl_2$	PhIO	alcohol, ketone acid, epoxide aldehyde	60 °C	[108,109]
$^6Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	CH_3CN	PhIO	epoxide, aldehyde	60 °C	[110]
$^4Q_4(RuH_2O)PW_{11}O_{39}$	alkene	CH_3CN	PhIO	epoxide, aldehyde	60 °C	[110]
$^4Q_5MnPW_{11}O_{39}$	alkene	CH_3CN/CH_2Cl_2	PhIO	epoxide	20 °C, argon	[100]

Table 2 (*continued*)

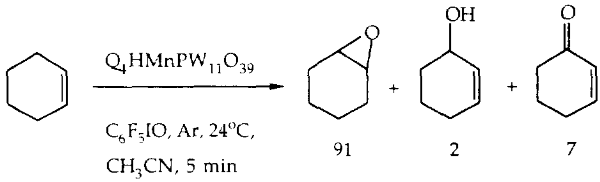
Catalyst[a]	Substrate	Solvent	Oxidant[b]	Products[c]	Comments	Reference
$^{7}Q_5(CrO)SiW_{11}O_{39}$	alkene	CH_3CN or C_6H_6	$(Cr^V=O)$	epoxide allylic alcohol[i] allylic ketone	50 °C, argon	[101]
$^{4}Q_4(CrO)PW_{11}O_{39}$	alkene	CH_3CN	$(Cr^V=O)$	epoxide allylic alcohol allylic ketone	50 °C, argon	[101]
$^{6}Q_4(CrO)PW_{11}O_{39}$	alkene	CH_3CN or C_6H_6	$(Cr^V=O)$	epoxide allylic alcohol allylic ketone	50 °C, argon	[101]
$^{4}Q_8CuP_2W_{17}O_{61}$	alkene	H_2O/CH_2Cl_2	NaClO	epoxide chloro/alcohol allylic alcohol allylic ketone ketone	24 °C, argon	[7,111]
$^{4}Q_7(\alpha_2\text{-}Fe^{III}P_2W_{17}O_{61})$	alkene	CH_3CN	H_2O_2	epoxide allylic alcohol allylic ketone	25 °C, N_2	[105]
$^{4}Q_8(\alpha_2\text{-}MBr)P_2W_{17}O_{61}$, $M=Mn$ or Fe	alkene	CH_3CN/CH_2Cl_2	PhIO	epoxide allylic alcohol allylic ketone	20 °C, argon	[100]
$^{4}Q_9(\alpha_2\text{-}MBr)P_2W_{17}O_{61}$, $M=Co$, Ni or Cu	alkene	CH_3CN/CH_2Cl_2	PhIO	epoxide	20 °C, argon	[100]
$^{7}Q_6MnSiW_{11}O_{39}$	alkylphenol	$C_6H_5CH_3$	O_2	dione, dimer	25 °C phase transfer	[112]
$^{7}Q_5(CrO)SiW_{11}O_{39}$	allylic alcohol	CH_3CN	$(Cr^V=O)$	allylic ketone	50 °C, argon	[101]
$^{4}Q_4RuPW_{11}O_{39}$	alcohol or aldehyde	H_2O	$KClO_3$	acid	25–75°C	[113]
$M^{II}PW_{11}O_{39}^{5-}$, $M=Fe$, Co or Ni	H_2S	H_2O	O_2	S(0)	pH 2–5 O_2 or N_2 293 K pH = 3–5.5	[114]

$MX^{n+}W_{11}O_{39}^{(10-n)-}$ $M = Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}$, Cu^{II} or Mn^{II}, $X = P^{5+}$ or Si^{4+}	H_2S	H_2O	O_2	S(0)	60 °C	[115]
$Na_5(FeH_2O)PW_{11}O_{39}$	NO, H_2S	H_2O	O_2	HNO_3, S	20 °C^j	[116,117]
$^7Q_5(CrO)SiW_{11}O_{39}$	triphenylphosphine	C_6H_6	$(Cr^V=O)$	triphenylphosphine oxide	25 °C, argon	[101]
2. Trisubstituted TMSP catalyst						
$H_6M_3PW_9O_{37}$, M = Fe or Cr	alkane	CH_3CN	O_2	alcohol, ketone	150 °C	[70,118]
$H_7Fe_2MPW_9O_{37}$, M = Ni, Mn, Co or Zn	alkane	CH_3CN	O_2	alcohol, ketone	150 °C	[70,118]
$^4Q_4H_6(Fe_2Ni(OAc)_3)PW_9O_{37}$	alkane	CH_3CN	O_2 or H_2O_2	alcohol, ketone	82 °C or 50 °C	[119]
$Q_4H_6(Fe_2Ni(OAc)_3)PW_9O_{37}$	alkene	CH_3CN	O_2	allylic alcohol allylic ketone epoxide	30 °C^k	[119]
$(Fe^{III})_3(SiW_9O_{37})^{7-}$	alkene	CH_3CN	H_2O_2	epoxide allylic ketone allylic alcohol	25 °C, N_2	[105]
$WZnM_2(ZnW_9O_{34})_2^{12-}$, M = Mn, Ni, Cu, Co or Fe	alkene	$ClCH_2CH_2Cl$	H_2O_2	epoxide allylic ketone	22 °C^l	[120]
$WMnMn_2(ZnW_9O_{34})_2^{12-}$ or $WCoCo_2(CoW_9O_{34})_2^{12-}$	alkene	$ClCH_2CH_2Cl$	H_2O_2	epoxide allylic ketone	22 °C^l	[120]
$WZnMn_2(ZnW_9O_{34})_2^{12}$	alcohol	$ClCH_2CH_2Cl$	H_2O_2	ketone	22 °C^l	[120]
$WCoMn_2(CoW_9O_{34})_2^{12-}$, $WZnZn_2(ZnW_9O_{34})_2^{12-}$ or $M_4(PW_9O_{34})_2$, M = Fe or Mn	alkene	$ClCH_2CH_2Cl$	H_2O_2	no rxn	22 °C^l	[120]
$^4Q_4H_6(Fe_2Ni(OAc)_3)PW_9O_{37}$	aldehyde	CH_3CN	O_2	acid	30 °C	[119]
$Na_{10}(Fe_3^{II}H_2O)_3X_2W_{18}O_{66}$, X = As, Se or Te	NO	H_2O	O_2	HNO_2	22 °C	[121]
3. Tetrasubstituted TMSP catalysts						
$^6Q_{10}M_4(B\text{-}PW_9O_{34})_2$, M = Ni or Fe	alkene	CH_3CN	H_2O_2	epoxide allylic alcohol allylic ketone	20 °C, argon	[7]
$^4Q_{10}Fe_4(B\text{-}PW_9O_{34})_2$,^{m} $^4Q_{10}Co_4(B\text{-}PW_9O_{34})_2$	alkene	CH_3CN	H_2O_2	epoxide allylic alcohol	20 °C, argon	[105,106]

Table 2 (*continued*)

Catalyst[a]	Substrate	Solvent	Oxidant[b]	Products[c]	Comments	Reference
$^4Q_{16}Ni_4(P_2W_{15}O_{56})_2$	alkene	H_2O/CH_2Cl_2	NaOCl	epoxide chloro/alcohol allylic alcohol allylic ketone, ketone	24 °C, argon	[7,111]
4. Electrocatalysis reactions						
$^4Q_5(RuH_2O)SiW_{11}O_{39}$	alkene	$H_2O/C_2H_4Cl_2$	$NaIO_4$, PbO_2 anode	aldehyde	60 °C, $NaIO_3$	[122]
$(CrO)PW_{11}O_{39}^{4}$ or $(CrO)P_2W_{17}O_{61}^{7-}$	alcohol	aq buffer	electrolysis	aldehyde	25 °C, argon	[123]
$(RuH_2O)PW_{11}O_{39}^{4-}$	sulfoxide	$H_2O/H_2SO_4/Na_2SO_4$		sulfone	[n]	[110]
$(Fe^{III}H_2O)XW_{11}O_{39}^{n-}$, X = Si, P, Ge or As	NO_2	aq buffer	electrolysis	NH_3	25 °C, argon	[124]
$(Fe^{III}H_2O)P_2W_{17}O_{61}^{7-}$	NO_2^-	aq buffer	electrolysis	NH_3	25 °C, N_2	[125]
$(Fe^{III}H_2O)SiW_{11}O_{39}^{5-}$	H_2O_2	aq buffer	electrolysis	H_2O	25 °C, N_2	[126]
$(Fe^{III}H_2O)P_2W_{17}O_{61}^{7-}$	H_2O_2	aq buffer	electrolysis	H_2O	25 °C, N_2	[125]

[a] $^4Q=(n\text{-}C_4H_9)_4N^+$; $^6Q=(n\text{-}C_6H_{13})_4N^+$; $^7Q=(n\text{-}C_7H_{15})_4N^+$. [b] TBHP = *tert*-butylhydroperoxide; *m*CPBA = *meta*-chloroperoxybenzoic acid; PhIO = iodosylbenzene; PFIB = pentafluoroiodosylbenzene; the oxochromium catalyst ($Cr^V=O$) was prepared by oxidation with NaOCl, H_2O_2 or PhIO. [c] no rxn = no reaction was observed; acid = carboxylic acid. [d] Isobutyraldehyde was added to the reaction. Several reactions were examined using the cobalt substituted catalyst and varying the oxidant (N_2 + PhIO; $N_2 + H_2O_2$), aldehyde (pivalaldehyde, butyraldehyde, acetaldehyde, valeraldehyde, benzaldehyde), and solvent ($CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, DMF, DMSO). All reactions yielded epoxide (except DMSO solvent). [e] Isobutyraldehyde or trimethylacetaldehyde was added to the reaction. [f] $Na_2S_2O_4$ (reductant) and tetrabutylammonium hydrogen sulfate (phase transfer agent) were added in an aqueous solution. [g] Sodium ascorbate (reductant) and tetrabutylammonium hydrogen sulfate (phase transfer agent) were added in an aqueous solution. [h] The reaction was performed in the presence of colloidal platinum on polyvinylpyrollidinone in ethanol/benzene under hydrogen and oxygen. [i] With some substrates, the allylic alcohol was not observed. [j] Membrane separation of $NaCO_3$ and the catalyst, removal of sulfur by filtration or centrifugation. [k] 2-Methylpropanal was added to the reaction solution. [l] The aerobic reaction was biphasic and run in the presence of methyltricaprylammonium chloride. [m] The reaction was evaluated in the presence of acid or base. The reaction was evaluated in different solvents, including propylene carbonate, acetone, chloroform, methyl t-butyl ether ($^6Q_{10}$ salt), toluene ($^6Q_{10}$ salt), t-butanol ($^6Q_{10}$ salt), and water (K_{10} salt). [n] Electrolyzed using a graphite thread anode (1.10 V).



(12)

As a generic class of compounds, TMSP complexes exhibit many of the attractive features of metalloporphyrins [5]. These include: (1) multidentate ligand systems that bind the d-electron transition metal ions in multiple oxidation states with sufficient strength that they are not lost. This can be critical, as oxygenation processes (Eq. (3) and (4) or Eqs. (3) and others in Fig. 3) and some other processes dictate oxidation state changes in the metal. As oxidation state changes usually result in significant changes in lability and other electronically controlled properties, it is often difficult for ligand systems to adequately retain the metal throughout a catalytic cycle. If the metal is lost (deligated), it usually precipitates rapidly as the transition metal oxide. While transition metal oxides can be quite active as heterogeneous oxidation catalysts at the temperatures typically used in such oxidation processes (often over 200 °C), they are effectively inactive for low temperature homogeneous catalytic oxidations. (2) Both metalloporphyrin and TMSP ligand systems can bind or activate substrates proximal to the active site, and both ligand systems can be reduced, which facilitates the activation of some oxidants and the quenching of various intermediates seen in oxidation processes. (3) The electronic structures (tendency to donate or accept electrons and relative energies of frontier orbitals) of both types of ligand systems can be altered by rational synthesis, and (4) both types of complexes can be rendered soluble in both polar and nonpolar media. TMSP complexes, unlike metalloporphyrins, however, are not susceptible to oxidative degradation (the rate of Eq. (11) in Fig. 3 is 0), and as a consequence, they continue to catalyze oxygenation and other oxidations for longer than metalloporphyrins or other conventional inorganic complexes with organic ligands. Last but not least, many TMSP complexes (unlike halogenated metalloporphyrins) are readily accessible and available in significant quantity in two-to-three-step high yield syntheses.

2.1.1. *Monosubstituted catalysts*

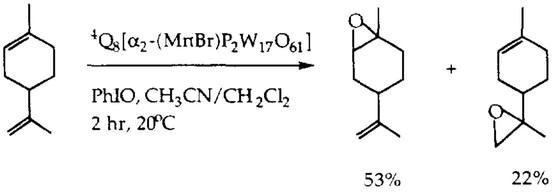
As shown in Table 2, a considerable number of reactions, and particularly those of monosubstituted TMSP catalysts with the Keggin structure, have been studied. The monosubstituted TMSP catalysts of formula $\mathrm{M}^{n+}\mathrm{XM}'_{11}\mathrm{O}_{39}^{7-n}$, where X = P or Si; M = Co, Mn, Cu, Fe, Cr, Ni, or Ru; and M′ = Mo or W, are the most thoroughly studied. Several oxidants and a wide range of substrates have been examined, leading to a range of oxygenated products. Since the solubility of the polyoxometalate can easily be adjusted with use of different counter cations, many solvents and combinations of solvents have been studied. We now describe some of these reactions. Again, it is unfortunate that most of these studies are descriptive and unsophisticated. Many contain insufficient information to establish either the actual catalyst(s) or the nature (mechanism) of the reactions themselves.

Not surprisingly, alkane oxidation reactions catalyzed by monosubstituted Keggin or Dawson polyoxometalates produce alcohol and ketone products under a wide variety of conditions. The oxidation of alkanes by O_2 facilitated by several TMSP complexes of the Keggin structure has been reported by Lyons and Ellis [70,93]. The addition of azide to an aqueous solution of $K_5CrPW_{11}O_{39}$, producing presumably the 1:1 adduct, $K_5CrPW_{11}O_{39}N_3$, led to a ~54-fold increase in rate from 14 to 762 turnover h^{-1}. Equal amounts of alcohol and ketone products were produced in both cases. More spectroscopic information would have been helpful in these studies (characterization of these catalysts was limited to elemental analysis, in some cases, and IR). Bressan and coworkers reported the homogeneous catalytic oxygenation of several alkanes in a two-phase system with the alkane in dichloromethane and the catalyst ($K_5Ru(H_2O)PW_{11}O_{39}$) and oxidant (NaClO or TBHP) in water [94]. Methylene groups were found to be oxygenated to secondary alcohols and then to the dominant ketone products. There has been controversy (vide infra) regarding the actual formulation of Ru-substituted polyoxometalates.

TMSP complexes have been documented to catalyze the oxidation of alkenes, under varying conditions, to give epoxides, allylic alcohols, allylic ketones, oxidative cleavage products, carboxylic acids, and aldehydes. Mizuno and coworkers studied the effect of several Keggin TMSP catalysts ($MPW_{11}O_{39}^{5-}$), several aldehydes, and different solvents on the aerobic oxidation of cyclohexene to epoxide (major product), and allylic alcohol and ketone (minor products) [102]. The order of TMSP activities was found to be Co (most active)$\gg$Mn$\geqslant$Fe$>$Cu$\geqslant$Ni (least active). Further study of the effect of aldehyde and solvent was conducted with the most active catalyst, $CoPW_{11}O_{39}^{5-}$ [102]. It was found that addition of aldehyde increases the catalytic activity of the system with the following order of effectiveness: pivalaldehyde $>$ isobutyraldehyde $\gg$ butyraldehyde $\approx$ acetaldehyde $>$ valeraldehyde $>$ benzaldehyde [102]. The catalytic activity of $CoPW_{11}O_{39}^{5-}$ was solvent dependent: chloroform (fastest rates)$\geqslant$dichloromethane$>$1,2-dichloroethane$\geqslant$acetonitrile$>$ *N,N*-dimethylformamide$>$dimethyl sulfoxide (slowest rates). It is likely that these reactions simply involve autoxidation of the aldehydes to the peracids which then epoxidize the alkenes either directly or with TMSP catalysis. While the authors mention that perisobutyric acid might be an intermediate in the oxidations, they did not do the control experiments involving alkene and peracid with and without the $CoPW_{11}O_{39}^{5-}$. If the main role of the TMSP is as a redox initiator of aldehyde autoxidation it would be more appropriate to view the complex as an initiator than as a catalyst.

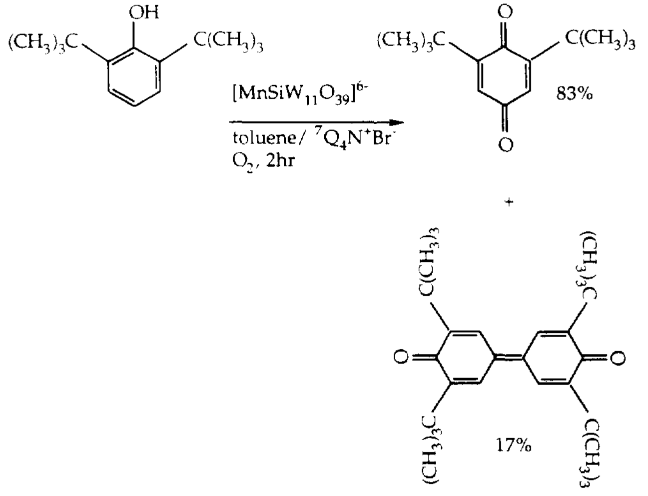
Neumann and Levin studied the effect of several reducing agents ($Na_2S_2O_4$, ascorbate, $NaBH_4$, or H_2/Pt) on the product selectivity when molecular oxygen is used as the oxidant and a TMSP, $MSiW_{11}O_{39}^{q-}$ (M $=Mn^{3+}$, Cu^{2+}, Co^{2+}, Fe^{3+}), is used as catalyst with an alkene substrate [104]. In general, allylic products were observed in the presence of sodium dithionate, epoxidation products in the presence of hydrogen/Pt, saturated alcohols in the presence of sodium borohydride, and no products in the presence of ascorbate. Neumann and coworkers also examined the alkene oxidation by $RuSiW_{11}O_{39}^{5-}$ with several oxidants [108,109]. In the case of styrene, sodium periodate oxidant produced exclusively the aldehyde oxidative cleavage product, while potassium persulfate produced primarily the carboxylic acid. Iodosylbenzene and TBHP produced cleavage, epoxidation, and oxidation products. The mechanism of oxidative cleavage by periodate catalyzed by $RuSiW_{11}O_{39}^{5-}$ was studied to a greater degree than nearly all other reports on TMSP catalysis (see Section 2.2). A concern in this, however, was the nature of the catalyst itself as two other groups subsequently provided evidence that the catalyst used by Neumann and Levin was more than likely a mixture of compounds. RuTMSP complexes, in part as a function of minimal lability of both Ru(III) and Ru(II), are far more difficult to prepare and purify than most, if not all, of the analogous first-row TMSP complexes. First, Rong and Pope provided the first (1992) definitive purification and characterization of a Ru polyoxometalate when they synthesized the $Ru^{III/II}PW_{11}O_{39}^{4-/5-}$ complexes, characterized several of their physical and spectroscopic properties, and reported a little catalysis (products from oxidation of *trans*-stilbene by iodosylbenzene). In this paper, they stated that the cyclic voltammogram of a sample of the Neumann and Levin "$RuSiW_{11}O_{39}^{5-}$" catalyst indicated that a mixture of species was present [110]. Subsequently (1993), Randall, Weakley and Finke also charged that the Neumann–Levin "$RuSiW_{11}O_{39}^{5-}$" was a mixture [127]. These workers reported the definitive characterization including an X-ray structure of an oxo-bridged diruthenium "bimetallic-porphyrin analog", $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]$ but no catalysis [127].

Mansuy, Finke, and coworkers examined the oxidations of alkenes and alkanes catalyzed by Wells–Dawson TMSP catalysts and compared the reactions to those catalyzed by analogous metalloporphyrins [100]. These TMSP complexes were as well characterized as any in the literature. In the case of (+)-limonene, the total epoxide yield was greater for the TMSP than the metalloporphyrin catalysts. As shown in Eq. (13), oxidation of (+)-limonene with the Mn(III) Wells–Dawson TMSP gave a 53% yield of 1,2-epoxide and a 22% yield of 8,9-epoxide.



(13)

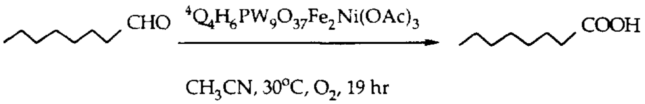
Other oxidations catalyzed by TMSP complexes include H_2S to S(0) by O_2 [114,115], and triphenylphosphine to triphenylphosphine oxide by $CrV(O)SiW_{11}O_{39}^{5-}$ [101]. The oxidation of alcohol and phenol substrates catalyzed by TMSP complexes, including the aerobic oxidation of hindered phenols facilitated by $MnSiW_{11}O_{39}^{6-}$, has been examined by Katsoulis and Pope (Eq. (14)) [112]. The type of products and yields observed in the latter reaction vary considerably with the hindered phenol used.



(14)

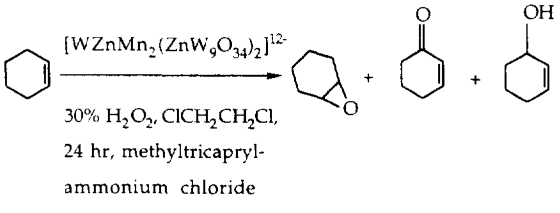
2.1.2. *Trisubstituted and tetrasubstituted catalysts*

Trisubstituted and tetrasubstituted TMSP catalysts have not been studied as extensively as the monosubstituted TMSP catalysts, as is evident from Table 2. One key reason for this is undoubtedly that the trisubstituted TMSP complexes are harder to synthesize in pure, unequivocally characterized form. One of the most heavily evaluated classes of trisubstituted TMSP complexes with respect to catalysis has been the complexes of the general formula $M_3PW_9O_{37}$, where $M_3 = Fe_2M'$ and $M' = Ni$, Fe, Mn, Co, or Zn first reported by Ellis and coworkers [70,118]. The free heteropolyacids were made by pyrolyzing the tetra-*n*-butylammonium salts (temperature not given). As many Keggin structures do not withstand temperatures necessary for such reaction, it would have been of interest and pertinence to have some information regarding changes in the catalyst after pyrolysis. The complexes were characterized primarily by elemental analysis [70]. Further work might permit one to distinguish $Fe_2MPW_9O_{37}$ from other possible formulations including 2/3 $Fe_3PW_9O_{37} + 1/3\ M_3PW_9O_{37}$. As expected, oxidation by O_2 of alkane substrates produced alcohols and ketones; alkenes produced allylic alcohols, allylic ketones and epoxides; and aldehyde produced carboxylic acid. Mizuno and coworkers examined the oxidation of octanal by O_2 as shown in Eq. (15) [119]. The catalyst was quite thoroughly characterized; the reactions themselves were less so. Lyons and coworkers studied the oxidation activity of a series of trisubstituted Keggin catalysts, $H_7Fe_2MPW_9O_{37}$, where M = Ni, Fe, Zn, Mn, or Co, with propane as substrate [70]. It is not at all unlikely that in both of the interesting studies of Lyons et al. [70] and Mizuno et al. [119] TMSP complexes may be functioning more as radical chain initiators than as true catalysts. The complexes probably function to catalytically break down intermediate peroxides (or peracids in the work of Mizuno and coworkers), and may be participating in or facilitating several processes simultaneously.



(15)

Another class of TMSP catalysts examined at length are sandwich-type compounds with a central unit of four edge-shared TMO_6 octahedra where TM is a first row transition ion, sandwiched between two B-$XW_9O_{34}^{9-}$ units, complexes first reported by Weakly and Tourné [128] (Fig. 2(C)) and sandwiched between two $P_2W_{15}O_{56}^{12-}$ units, complexes first reported by Finke and Droege [129] (Fig. 2(D)). Hill and coworkers first reported the oxidation of alkenes by H_2O_2 with tetrasubstituted TMSP catalysts. Epoxidation and allylic oxidation products were observed in all cases. In the case of $^6Q_{16}[(Ni^{II})_4(P_2W_{15}O_{56})_2]$ as the catalyst, oxidation of cyclohexene resulted in chlorinated products doubtless derived from attack of intermediate radicals on the solvent (a CH_2Cl_2/H_2O solvent system was used). These products were eliminated if the solvent was changed to benzene [7]. Little mechanistic work was reported. Khenkin and Hill reported the synthesis of and the effective H_2O_2-based epoxidation catalyzed by the Fe_4 complexes, $[Fe_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Fe_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ [106]. These Fe_4 complexes produced epoxides in high selectivity while other Fe-containing TMSP complexes did not, consistent with quite distinct dominant mechanisms with the different FeTMSP catalysts. H_2O_2-based epoxidation of cyclohexene catalyzed by $Fe^{II}PW_{11}O_{39}^{5-}$, $[(Fe^{III})_3(SiW_9O_{37})]^{7-}$ and $[Fe_4(PW_9O_{34})_2]^{10-}$ proceeded in 7, 49, and 90% selectivity, respectively (all reactions were homogeneous in CH_3CN/H_2O solution under N_2 at 25 °C) [105]. Later Neumann and Gara examined similar H_2O_2-based epoxidations catalyzed by the isostructural but more highly charged sandwich complexes comprising a central, $WM'M_2$ unit (two M ions opposite each other and on the outside of the complex) sandwiched between two B-$XW_9O_{34}^{12-}$ units, X = Zn(II) or Co(II), complexes first prepared by Tourné and coworkers [130]. The complex $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ was the best of these catalysts and superior to the Fe_4 sandwich complexes of Khenkin and Hill [120]. A variety of alkene substrates were investigated. In the case of cyclohexene, epoxidation was the primary mode of oxidation at 2 °C, but allylic oxidation was the primary mode of oxidation at 70 °C (Eq. (16)) [120].

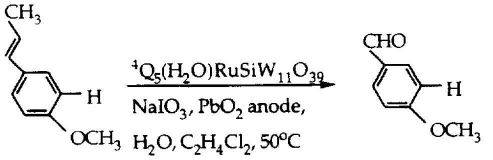


(16)

at 2°C	1450	5	0
at 70°C	10	1340	430

2.1.3. *Electrocatalysis reactions*

Several papers have been published addressing the electrochemical properties of TMSP catalysts. Toth and Anson have reported the electrochemical behavior of $FeXW_{11}O_{39}^{5-}$ where X = Si, Ge, P, or As, determined that changes in the central heteroatom result in changes in the formal Fe^{III}/Fe^{II} potential, and evaluated the effect of pH and ionic strength [131]. Later, Toth and Anson evaluated the electrochemical reduction of nitric oxide and nitrite to ammonia with $(Fe^{III}H_2O)XW_{11}O_{39}^{n-}$, where X = Si or Ge ($n = 5$), P or As ($n = 4$), and found the catalysts to have long-term durability [124]. Subsequently, they reported the electrochemistry and redox chemistry of $(Fe^{III}H_2O)SiW_{11}O_{39}^{5-}$ in the presence of OH and H_2O_2 [126]. Dong and Liu studied the electrocatalytic reduction of NO_2^- and H_2O_2 by $(Fe^{III}H_2O)P_2W_{17}O_{61}^{7-}$ [125]. Rong and Pope reported the electrocatalytic oxidation of sulfoxide to sulfone by $Ru^{V}(O)PW_{11}O_{39}^{4-}$ with greater than 90% current efficiency [110]. Most recently, Rong and Anson found that benzyl or ethyl alcohol was slowly oxidized to the aldehyde by $(CrO)PW_{11}O_{39}^{4-}$ or $(CrO)P_2W_{17}O_{61}^{7-}$ generated electrochemically [123]. Finally, Steckhan and Kandzia reported the electrochemical cleavage of styrene derivatives to benzaldehydes catalyzed by $RuSiW_{11}O_{39}^{5-}$ in a multiphase system (Eq. (17)) [122]. The problematic issue of purification and characterization of such Ru polyoxoanions is, again, noted [110,127].



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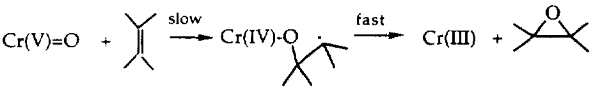
2.2. *Mechanistic overview of reactions*

To date there have been several reports that address the mechanism of TMSP catalyst reactions at the level of organic product distributions and limited structure reactivity relationships and very few reports that address the mechanism at the more involved level of insightful kinetics and detailed evaluation of elementary processes. A majority of the papers, in general, don't go significantly beyond the trivial identification of organic oxidation products after a set reaction time or after consumption of a set amount of oxidant. From the limited mechanistic data that are available to date, however, four points are apparent. First, the mechanism for the TMSP catalyzed oxidation of hydrocarbon substrates alone appears to vary considerably with both the metal and the oxygen donor just as it does in the analogous oxidations catalyzed by metalloporphyrin, Schiff–base complexes, and other more conventional transition metal complexes. The word "appears" was carefully chosen as there are insufficient data at present to say anything definitive about trends in mechanism.

Second, in no case have the O_2-based oxidations been studied adequately. Next to nothing is known in detail about the nature of the reactions. Given the vast literature on homogeneous metal catalyzed O_2-based oxidation (autoxidations and others) and the chemistry in these reports on TMSP facilitated O_2 oxidations, it is likely that the latter reactions involve both conventional radical chain components (not shown in Fig. 3) and, in some cases, oxygenation components (Eq. (3) and reoxidation processes in Fig. 3). A principal role of the TMSP complexes in the radical chain component of these O_2-based oxidations is doubtless as an initiator and/or a catalyst for breakdown of peroxide intermediates. As a redox initiator only, which appears to be their function in some cases, they are not technically catalysts and hence our deliberate use above of the verb "facilitate" rather than "catalyze". The TMSP complexes may also modulate various reactions of radical intermediates. Further delineation of these reactions must await the results of quantitative investigations. A caution should be articulated here that an attempt to use radical scavengers to quantify or even qualitatively eliminate the radical-chain component in these TMSP facilitated O_2 oxidations could be problematical. Scavengers, as they often do in reactions involving short radical chains, may have no effect in these reactions. Alternatively, scavengers are likely to bind to the TMSP or otherwise alter the chemistry.

Third, the first step in TMSP catalyzed oxidation of organic substrate by any oxygen donor is the association or binding of the oxygen donor and/or the substrate to the TMSP itself. Despite the fact that binding numbers (stoichiometric ratios of donor or substrate to TMSP) and the binding constants can be assessed by straightforward spectroscopic (thermodynamic) and kinetics studies, only one such study has been conducted under conditions similar to those used in the catalytic oxidation reactions themselves. Finke and co-workers reported the equilibrium constants for association of four different bases, *N*-methylimidazole, pyridine, triphenylphosphine, and Br^-, to α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ [132]. Some quantitative association chemistry involving Keggin-type TMSPs has been reported by Weakley [133] (binding of SCN^-, $(NH_2)_2CS$, and various pyridines to $Co^{II}W_{11}O_{39}^{5-}$, X = B, P, and As in water) but none with ligands pertinent to catalytic oxidation. A difficulty in assessing equilibrium association constants and binding numbers appears as a consequence of the assessment of results from the similarity in the chromophores of ligand bound and ligand free forms of the TMSP. This may preclude ready measurement.

Fourth, only two studies in the literature address, to a significant extent, the mechanism of TMSP catalyzed organic substrate oxidations at the level of rate constants and quantitative elementary processes. The first, by Neumann and Abu-Gnim, investigates oxidative cleavage of alkenes by IO_4^- catalyzed by $RuSiW_{11}O_{39}^{x-}$ [108]. While there is ambiguity as to exactly what was being measured in some kinetics plots and uncertainty about the precise formulation of the catalyst (vide supra) [110,127], the mechanistic inferences in this work follow from the data. Product generation involves rate limiting reaction of a complex between alkene substrate, a water molecule and an oxidized form of the Ru TMSP. This strong paper contributes significantly to our understanding of catalysis by TMSP complexes. In the other study, Khenkin and Hill demonstrated that $S = 1/2$ d^1 oxo Cr(V) complexes, $(OCr^V)X^{n+}W_{11}O_{39}^{(9-n)^-}$, $X^{n+} = P^V$ and Si^{IV}, first reported by Katsoulis and Pope [134], catalyze the oxidation of organic substrates (alkenes, alkanes, alcohols, and one phosphine, Ph_3P) by a variety of oxidants (OCl^-, H_2O_2, or iodosylbenzene). More significantly, however, they were able to study one exemplary reaction in greater mechanistic detail than any other TMSP catalyzed reaction. The in-depth mechanistic analysis was facilitated by the ability to directly monitor the actual form of the TMSP complex, the oxo Cr(V) specie itself, involved in attack on substrate. The rate law and seven other lines of evidence were consistent with oxo transfer from the complex to the substrate proceeding by a rate limiting radical addition of the oxo unit to the alkene, Eq. (18) [101]. Electron transfer, concerted oxo transfer, carbocation and several other mechanisms were ruled out.



(18)

A great deal of work, particularly on the dynamic and mechanistic front, is needed on TMSP catalyzed reactions if their potential utility in conventional areas (e.g. commodity products from selective oxidation) and other areas (e.g. asymmetric transformations and modification of high technology materials, etc.) is to be fully defined.

3. Mixed addenda polyoxometalates

3.1. Homogeneous catalytic reactions

Mixed addenda polyoxometalates are typically formed from the substitution of one or more tungsten(VI) or molybdenum(VI) ions in Keggin, Wells–Dawson, and other prominent structural families of heteropolyanions (vide supra: Figs. 1 and 2). Many mixed addenda polyoxometalates such as the heavily investigated $PMo_{10}V_2O_{40}^{5-}$ are mixtures of positional isomers. In the case of disubstituted Keggin complexes, such as $PMo_{10}V_2O_{40}^{5-}$, there are 66 possible ways of arranging the constituent ions, which after allowance for degeneracy leads to five distinct isomers [135]. In general for x substituted metal ions, M′, in a Keggin structure $YM'_xM_{12-x}O_{40}^{(3+x)-}$, Y = the heteroatom, there are $12!/x!(12-x)!$ possible ways to arrange the constituent ions [135]. The lability of these different positional isomers depends on the particular complex (for example, the di- or polysubstituted polymolybdates are more labile than the structurally analogous di- or polysubstituted polytungstates) but equilibration is usually achieved quickly under the conditions used in homogeneous catalysis. Quantitative studies documenting the speciation thermodynamics of mixed addenda polyanions, and particularly recent studies by Pettersson and co-workers on V-containing Keggin systems have provided data of direct value for optimization of catalysis [136–138]. Grate and co-workers at Catalytica have used just such seminal information to optimize promising $PV_xMo_{12-x}O_{40}^{(3-x)-}/Pd$ systems (vide infra) [137,139–141].

Mixed addenda polyoxometalates already occupy roles of central importance in both homogeneous and heterogeneous catalysis and in both oxidation and acid-catalyzed reactions. The largest number of papers in the homogeneous catalytic area involve oxidation. Many of the desirable attributes of mixed addenda polyoxometalates were addressed in the general sections above. These include ease in preparation, low cost, robustness (both thermal and oxidative), and solubility, depending on counterion, in media from water to hydrocarbons. The mixed addenda polyoxometalates used most commonly in homogeneous oxidation processes are those that contain vanadium for the simple reason that vanadium is the most strongly oxidizing addenda element.

Another attractive feature of homogenous catalytic oxidation by mixed addenda polyoxometalates is that they can function by the general two-step oxidation (Eqs. (8) and (9) in Fig. 3), as well as by other mechanisms. For those reactions proceeding by the Eqs. (8) and (9), the ground state redox potentials of the complexes are crucially important. These potentials can be controlled by several features enumerated in Section 1.2.2. The higher the molecular charge, the more negative the potential, and the less facile is oxidation of substrate, Eq. (8) and the more facile is reoxidation of the reduced polyoxometalate ($M=O_{red}$), Eq. (9). While numerous reports have presented and analyzed useful data on redox potentials of polyoxometalates, a more sophisticated and comprehensive study that would take into account activity coefficients and ion pairing is lacking (see Section 6). Such a study would perforce be fairly substantial in size and would greatly augment the predictability of redox processes involving mixed addenda polyoxometalates. Table 3 summarizes the key papers since 1988 involving homogeneous catalysts by mixed addenda polyoxoanions. For elaboration of reactions in this class reported prior to this date, one is again referred to the reviews cited earlier.

3.1.1. Oxidation reactions

As shown in Table 3, the majority of the mixed addenda polyoxometalates studied are polymolybdovanadates and polytungstovanadates; however, a few examples of tungstoniobates and tungstomolybdates are given. Included in Table 3 are also the parent (non-mixed-addenda) polyoxometalate catalysts to compare with their mixed addenda counterparts. In general, for the oxidation of alkanes by O_2, the reactions containing polytungstovanadate or polymolybdovanadate mixed addenda catalysts exhibited higher rates of reaction than the parent polytungstate or polymolybdate catalysts [93]. Neumann and Levin examined the mechanism of the aerobic oxidative dehydrogenation of α-terpinene to *p*-cymene catalyzed by the mixed addenda polyoxometalate, $H_5PMo_{10}V_2O_{40}$ (Eq. (19)) [143]. Kinetic and spectroscopic (UV-vis, ESR, ^{31}P NMR, and IR) studies led to the conclusion that oxidative dehydrogenations take place by formation of an intermediate catalyst-substrate electron-transfer complex. After completion of the step involving substrate oxidation and catalyst reduction (analogous to Eq. (8) in Fig. 3), the catalyst is reoxidized via a proposed μ-peroxo intermediate whereby the primary oxidant, molecular oxygen, undergoes a four-electron reduction to water [143].

Table 3
Reactions catalyzed by mixed addenda polyoxometalate complexes

1. Oxidation reactions

Catalyst[a]	Oxidant[b]	Solvent[c]	Substrate	Products[d]	Comments[e]	Reference
$H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_{11}PMo_4V_8O_{40}$, $H_9PW_6V_6O_{40}$ or $K_5PW_{11}VO_{40}$	O_2	CH_3CN, or $AcOH/H_2O/C_6H_5Cl$	alkane	alcohol, ketone	150 °C	[70,93,118]
$H_6PW_9V_3O_{40}$ or $H_7PMo_8V_4O_{40}$	O_2	$AcOH/H_2O/C_6H_5Cl$	alkane	alcohol, ketone	100 °C	[93]
$K_3PMo_{12}O_{40}$ or $K_4SiMo_{12}O_{40}$	O_2	$AcOH/H_2O/C_6H_5Cl$	alkane	no rxn	150 °C	[93]
${}^4Q_9P_2W_{15}Nb_3O_{62}$	O_2	CH_2Cl_2	alkene	no rxn	38 °C	[142]
$H_5PMo_{10}V_2O_{40}$	O_2	CH_3CN	cyclic diene	aromatic derivative	25 °C	[143]
$(NH_4)_5H_4PW_6V_6O_{40}$, $(NH_4)_3PW_{12}O_{40}$, $(NH_4)_3PMo_{12}O_{40}$ or $(NH_4)_7HPW_8V_4O_{40}$	O_2	$ClCH_2CH_2Cl$	alkene aldehyde	epoxide	25 °C	[144]
$H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$	O_2	$ClCH_2CH_2Cl$	alkene aldehyde	no rxn	25 °C	[144]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$ClCH_2CH_2Cl$	aldehyde	acid	25 °C	[144]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$ClCH_2CH_2Cl$	ketone aldehyde	ester	25 °C	[144]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$ClCH_2CH_2Cl$	thianthrene 5-oxide, aldehyde	thianthrene dioxides	25 °C	[144]
$H_{3+n}PMo_{12-n}V_nO_{40}$, $n=2$, 4 or 6	O_2	$AcOH/H_2O$, CH_3OH/H_2O, CH_3CN/H_2O, $(CH_3)_2CO/H_2O$, CH_2Cl_2 or $CHCl_3$	alcohol[f]	quinone[f]	50 °C	[145,146]

$H_5PMo_{10}V_2O_{40}$	O_2	*n*-hexanol or CH_3CH_2OH	dialkyl phenol	diphenoquinone	60 °C	[143,147]
$H_6PMo_9V_3O_{40}$	O_2	C_6H_6	ketone	alcohol^g	70 °C	[148]
$H_5PMo_{10}V_2O_{40}$	O_2	CH_3CN, H_2O or $AcOH/H_2O$	α-substituted cyclic ketone	ketoacid	60 °C^h	[149–151]
$H_{3+n}PMo_{12-n}V_nO_{40}$, $n=0–3$	O_2	CH_3CN or substrate	benzylic ketone	acid benzaldehyde	20 °C^i	[150]
$H_{3+n}PW_{12-n}V_nO_{40}$, $n=0–1$	O_2	CH_3CN or substrate	benzylic ketone	acid benzaldehyde	20 °C^j	[150]
$H_7PMo_8V_4O_{40}$	O_2	H_2O	α-substituted cyclic ketone	ketoacid	60 °C	[151]
$^4Q_5PMo_{10}V_2O_{40}$	O_2	CH_3CN	α-substituted cyclic ketone	no rxn	60 °C	[151]
$H_5PMo_{10}V_2O_{40}$	O_2	CH_3CN, H_2O, ^{t}BuOH, C_2H_5OH, $AcOH/H_2O$	cyclic ketone	acid	65–70 °C	[151]
$H_7PMo_8V_4O_{40}$	O_2	$AcOH/H_2O$	cyclic ketone	acid	70 °C	[151]
$H_6PMo_9V_3O_{40}$	O_2	C_6H_6 or CH_3OH	ester	dienone^k lactone	70 °C	[148]
$(NH_4)_5H_4PMo_6V_6O_{40}$, $(NH_4)_5H_4PW_6V_6O_{40}$, $(NH_4)_3HPMo_{11}VO_{40}$, $H_4PMo_{11}VO_{40}$, $H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$	O_2	$C_6H_5CH_3$	benzylamine	Schiff-base imine	100 °C	[152]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$ClCH_2CH_2Cl$ or CH_3CN	benzylamine	Schiff-base imine	reflux	[152]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$C_6H_5CH_3$	isochroman	3,4-dihydro-isocoumarin	100 °C	[152]
$(NH_4)_5H_4PMo_6V_6O_{40}$	O_2	$C_6H_5CH_3$	indan	1-indanone	100 °C	[152]
$K_{14}NaP_5W_{30}O_{110}$, $K_7PW_{11}O_{39}$ or $K_8SiW_{11}O_{39}$	O_2	H_2O	H_2S	S(0)	60 °C	[115]
$H_5PMo_{10}V_2O_{40}$	O_2/HBr	$ClCH_2CH_2Cl$ tetraglyme^l	phenolic compound	*p*-bromo-derivative	20 °C	[153]

Table 3 (*continued*)

Catalyst[a]	Oxidant[b]	Solvent[c]	Substrate	Products[d]	Comments[e]	Reference
$H_5PMo_{10}V_2O_{40}$	O_2/HBr	$ClCH_2CH_2Cl$ tetraglyme[l]	alkene	vicinal dibromide	20 °C	[153]
$H_5PMo_{10}V_2O_{40}$	O_2/HBr	$ClCH_2CH_2Cl$ tetraglyme[l]	ketone	α-bromo-ketone	20 °C	[153]
$H_5PMo_{10}V_2O_{40}$, $H_5PW_{10}V_2O_{40}$, $H_4PMo_{11}VO_{40}$ or $H_6SiMo_{10}V_2O_{40}$	H_2O_2	CH_3COOH	alkyl aromatic	ketone acetate	110 °C or 60 °C	[154,155]
$H_3PMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$	H_2O_2	CH_3COOH	alkyl aromatic	ketone	110 °C or 80 °C	[154,155]
$H_5PMo_{10}V_2O_{40}$	H_2O_2	DMF, CH_3OH or formic acid	alkylbenzene	ketone	60 °C	[155]
[6]$Q_4PMo_{10}V_2O_{40}$	H_2O_2	$ClCH_2CH_2Cl$	alkylbenzene	ketone	60 °C	[155]
$H_5PMo_{10}V_2O_{40}$	H_2O_2	CH_3CN, ethylene glycol, $(CH_3)_2CO$ or sulfolane	alkylbenzene	ketone alcohol	60 °C	[155]
$H_5BW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ or $H_6P_2W_{18}O_{62}$	H_2O_2	$CHCl_3$	alkene	no rxn	60 °C, PTA	[156]
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $K_4W_{10}O_{32}$, $(NH_4)_{10}H_2W_{12}O_{42}$ or $(NH_4)_6Mo_7O_{24}$	H_2O_2	$CHCl_3$	alkene	epoxide	60 °C, PTA	[156]
[4]$Q_6H_2Si_2W_{18}Nb_6O_{77}$	H_2O_2	CH_3CN	alkene	no rxn	82 °C	[157]
[4]$Q_4Na_3PW_{11}O_{39}$	H_2O_2	CH_3CN	alkene	epoxide	20 °C	[106]
[4]$Q_3PW_{12}O_{40}$ or [4]$Q_5H_2PW_{11}O_{39}$	H_2O_2	CH_3CN	alkene	epoxide	35 °C, argon	[107]
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $K_4SiMo_{12}O_{40}$,	H_2O_2	tributyl phosphate solution	alkene	epoxide aldehyde, diol	35 °C	[158]

$H_4GeMo_{12}O_{40}$, $H_3PMo_{10}W_2O_{40}$ or $H_5PMo_{10}V_2O_{40}$						
$^4Q_6H_2Si_2W_{18}Nb_6O_{77}$	H_2O_2	CH_3CN	allylic alcohol	triol	82 °C	[157]
$H_3XM_{12}O_{40}$ or $Na_3PM_{12}O_{40}$, X = P or Si, M = W or Mo	H_2O_2	CH_3CO_2H	phenol[m]	3 products[n]	30 °C, N_2	[159,160]
$H_3PMo_{12}O_{40}$, $H_3SiMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$	H_2O_2	CH_3CO_2H, CH_3OH, CH_3CN or HCO_2H	3,4,5-trimethoxy-toluene	2,6-dimethoxy-*p*-benzoquinone	30 °C, N_2	[161]
CWP	H_2O_2	$CHCl_3$	diol	α-hydroxy ketone	reflux	[37]
$^4Q_6H_2Si_2W_{18}Nb_6O_{77}$	H_2O_2	CH_3CN	maleic acid	diol[o]	82 °C	[157]
CWP or $H_3PW_{12}O_{40}$	H_2O_2	$CHCl_3$, ^tBuOH or CH_3OH[p]	aniline	nitrosobenzene nitrobenzene	25 °C	[162]
CWP	H_2O_2	$CHCl_3$	amine	*N*-oxide	25 °C	[38]
CWP or CMP	H_2O_2	$CHCl_3$	sulfide	sulfoxide, sulfone	25 °C	[163]
$^4Q_2H_4[CH_3C(CH_2O)_3P_2W_{15}V_3O_{59}]$	TBHP, H_2O_2 or PhIO	CH_3CN	thioether	sulfoxide	25° C, argon	[164]
$^4Q_5H_4P_2W_{15}V_3O_{62}$, $^4Q_6P_2W_{18}O_{62}$ or $^4Q_5H[CH_3C(CH_2O)_3P_2W_{15}V_3O_{59}]$	TBHP	CH_3CN	thioether	sulfoxide	25 °C	[164]
$H_6PW_9V_3O_{40}$, $H_5PMo_{10}V_2O_{40}$, $Q_{(5-x)}H_xPMo_{10}V_2O_{40}$, $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$	TBHP	CH_3CN	thioether	sulfoxide	25 °C, argon	[165]
$H_3PM_{12}O_{40}$ or $H_4SiM_{12}O_{40}$, M = W or Mo	TBHP	CH_3COOH	*p*-phenols	peroxy ketone quinone substrate dimer	30 °C	[166]

Table 3 (*continued*)

2. Acid catalyzed reactions

Catalyst[a]	Other acids[b]	Solvent[c]	Substrate	Products[d]	Comments[e]	Reference
$H_mXW_{12}O_{40}$ (X = P, Si, Ge, B or Co) or $H_6P_2W_{18}O_{62}$	PTS/H_2SO_4	IBP	IBP	alkene, acid	128 °C, N_2	[167]
$H_mXW_{12}O_{40}$ (X = P, Si, Ge, B or Co) or $H_6P_2W_{18}O_{62}$	PTS/H_2SO_4	IBP	IBP CH_3COOH	ester exchange[q]	70 °C, N_2	[167]
$H_mXW_{12}O_{40}$ (X = P, Si, Ge, B or Co) or $H_6P_2W_{18}O_{62}$	PTS/H_2SO_4	IBP	IBP *n*-propyl alcohol	ester exchange[r]	70 °C, N_2	[167]
$H_mXW_{12}O_{40}$ (X = P, Si, Ge, B or Co) or $H_6P_2W_{18}O_{62}$	PTS/H_2SO_4	isobutyl alcohol	propionic acid	isobutyl propionate	70 °C, N_2	[167]
$H_3PW_{12}O_{40}$	-	CH_3CN or CH_2Cl_2 CH_2Cl_2	17-α-hydroxy-progesterone	17-α-capronate, 3,17-α-dicapronate	40 °C[s]	[168]
$(NH_4)Mo_7O_{24}$	-	H_2O, ^iPrOH, dioxane, THF or CH_3CN	D-mannose	D-glucose	45–85 °C	[169,170]
$H_mXW_{12}O_{40}$, X = P, Si, Ge, B, Fe or Co	-	substrate	isobutyl propionate	not available	-	[171]
$H_3PM_{12}O_{40}$ (M = Mo or W) or $H_4SiW_{12}O_{40}$	-	substrate, hexane or diethyl ether	aldehyde	trioxane	25°C or −12 °C, O_2	[172]
$H_3PM_{12}O_{40}$ (M = Mo or W) or $H_4SiW_{12}O_{40}$	-	substrate	aliphatic aldehyde	2,4,6-trialkyl-1,3,5-trioxane	phase separation observed	[173]

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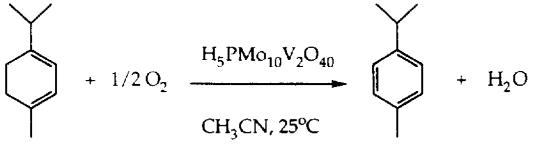
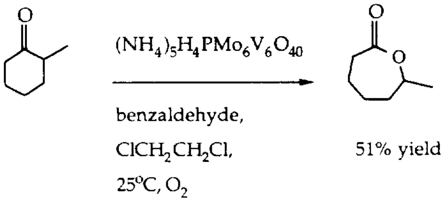
[a] $^4Q = (n\text{-}C_4H_9)_4N^+$; $^6Q = (n\text{-}C_6H_{13})_4N^+$; CWP = a catalyst prepared in advance of formula $(CP)_3PW_{12}O_{40}$; CMP = a catalyst prepared in advance of formula $(CP)_3PMo_{12}O_{40}$; CP = cetylpyridium cation. [b] TBHP = tert-butylhydroperoxide; PhIO = iodosylbenzene; PTS = *p*-toluenesulfonic acid. [c] AcOH = acetic acid; substrate = the substrate was also used as the solvent; ^iPrOH = iso-propanol; ^tBuOH = t-butanol; DMF = *N*,*N*-dimethylformamide; IBP = isobutyl propionate.

[d] acid = carboxylic acid; no rxn = no reaction was observed. [e] PTA = phase transfer agent (Q^+Cl^- = Arquad 2HT). [f] Alcohol = 2,3,6-trimethylphenol; quinone = 2,3,5-trimethyl-1,4-benzoquinone (also 2,2′,3,3′,6,6′-hexamethyl-4,4′-biphenol is produced as a byproduct). [g] The 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl) butan-2-one as substrate yields 4-hydroxy-4-(3-oxobutyl)-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one and *p*-benzoquinone. [h] When 2-methylcyclohexanone was used as substrate and acetonitrile or $AcOH/H_2O$ as solvent, 6-oxoheptanoic acid was produced as the major product with acetic acid and cyclopentanone as minor products. [i] Benzoic acid, an α-diketone, and *trans*-stilbene were produced as minor products with $n = 1–3$. [j] For $n = 0$, only trace amounts of products were observed. For $n = 1$, benzoic acid, a dione and *trans*-stilbene were produced as minor products. [k] The substrate, methyl ester of β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid, yields *p*-benzoquinone, spirolactone, dienone, and quinol. [l] Tetraglyme was used as a complexing agent to enable dissolution of $PMo_{10}V_2O_{40}^{5-}$ in its acidic form in nonpolar organic solvents [153]. Several other complexing agents were examined and are given in the original literature. [m] For example, when the substrate used was 2,6-di-*tert*-butyl-4-methylphenol. [n] The products were 2,6-di-*tert*-butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one, 2,6-di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, and 2,6-di-*tert*-butyl-*p*-benzoquinone. [o] (±)-$HO_2CCH(OH)CH(OH)CO_2H$. [p] In the case of methanol solvent, only nitrosobenzene is observed as a product. [q] Ester exchange of IBP with acetic acid. [r] Ester exchange of IBP with *n*-propyl alcohol. [s] $(AmCO)_2O$ was added as a reactant.



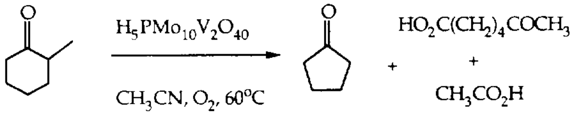
(19)

Ishii and coworkers have reported, but not mechanistically investigated, a number of provocative and synthetically interesting reactions involving oxidation of alkenes to epoxides, aldehydes to carboxylic acids, thianthrene 5-oxide to thianthrene dioxides, and cyclic ketones to esters with O_2 in the presence of an aldehyde and mixed addenda polyoxometalates [144]. Typical heteropoly acids with the Keggin structure proved to be inert under the reaction conditions. In the case of alkenes, reactions run in the absence of aldehyde yielded no products. An example of lactone formation is shown in Eq. (20) [144]. These reactions may or may not simply involve polyoxometalate initiated autoxidation. The mechanisms of these reactions are admittedly not a major interest to these authors [43].



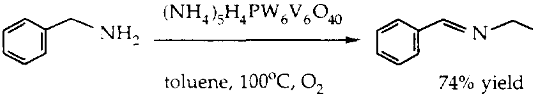
(20)

Kozhevnikov and coworkers obtained 2,3,5-trimethyl-1,4-benzoquinone from oxidation of 2,3,6-trimethylphenol by O_2 in the presence of molybdovanadate acids, $H_{3+n}PMo_{12-n}V_nO_{40}$, in AcOH/$H_2O$ [145,146]. Brégeault and coworkers studied the oxidation of ketones by dioxygen catalyzed by several mixed addenda polyoxometalates [149–151]. Substituted cycloalkanones, 1-phenylalkanones, and open-chain ketones are oxidatively cleaved by $H_5PMo_{10}V_2O_{40}$ under very mild conditions to give carboxylic acid, ester, α-diketone, and aldehyde products [149,150]. Solvent effects were studied for the reaction shown in Eq. (21) [151]. In AcOH/H_2O, Eq. (21) gives 6-oxoheptanoic acid with 90% yield and 99% conversion.



(21)

Ishii and coworkers reported the O_2 oxidation of benzylic compounds facilitated by mixed addenda polymolybdovanadates [152]. For example, benzylamine is oxidized to the corresponding imine using a series of mixed addenda polyoxometalates and simple metallophosphates. A representative reaction is shown in Eq. (22). All mixed addenda polyoxometalates, $PM_{12-n}V_nO_{40}^{(3+n)-}$ (M = W or Mo; n = 1, 2, or 6), catalyze the conversion of benzylamine to the imine in good yield, whereas the simple Keggin complex, $PM_{12}O_{40}^{3-}$, shows very little activity. Aliphatic primary amines are oxidized with low selectivity due to subsequent oxidation of the initial products. Oxidation of isochroman to 3,4-dihydroisocoumarin and indan to 1-indanone proceeds in 88% and 64% yields, respectively [152].



(22)

Harrup and Hill [115] have reported polyoxometalate-based catalytic systems for the effective and selective aerobic oxidation of H_2S to S(0), a reaction currently catalyzed by chelated Fe complexes in industry [174–177] (Eq. (23)). $K_5ZnPW_{11}O_{39}$, α-$K_8SiW_{11}O_{39}$, α-$K_6ZnSiW_{11}O_{39}$ and $K_{14}[NaP_5W_{30}O_{110}]$ are effective catalysts for Eq. (23) in aqueous solution exhibiting 40, 29, 21 and 7.4 turnovers, respectively at 60 °C with 1.1 atm O_2 for 24 h in a sealed, constant pressure system.

$$H_2S + 1/2O_2 \rightarrow H_2O + 1/8S_8 \tag{23}$$

Under these same conditions, $K_7PW_{11}O_{39}$ produces 50 turnovers and partially decomposes while sulfide quantitatively demetalates many substituted Keggin complexes, Eq. (24). The rate law for oxidation of HS^- by $[NaP_5W_{30}O_{110}]^{14-}$ borax buffer,

$$H_2S + X^{n+}MW_{11}O_{39}^{(10-n)-} \rightarrow MS + X^{n+}W_{11}O_{39}^{(12-n)-} + 2H^+ \tag{24}$$

where M = Fe(II), Co(II), Ni(II), or Cu(II)

and X^{n+} = P(V) or Si(IV).

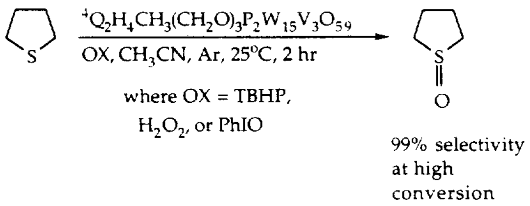
(pH 8.5 $[[NaP_5W_{30}O_{110}]^{14-}] = 2.0$ mM, [substrate] = 2.6 mM, 298 K) is $+d[[NaP_5W_{30}O_{110}]^{15-}] = [HS^-][[NaP_5W_{30}O_{110}]^{14-}]_2$ with a complex pH dependence that follows from the acid–base chemistry of the reactants. A comparison of Eq. (23) catalyzed by $[NaP_5W_{30}O_{110}]^{14-}$ versus the chelated Fe compounds used industrially indicates that for $[NaP_5W_{30}O_{110}]^{14-}$ the reaction is slower initially, lasts far longer since the catalyst is not degraded, and produces higher purity S_8 (>99.5% for the polyoxometalate versus 89.8% for $Fe^{III}(EDTA)^-$) [115].

Several groups have done research with H_2O_2/mixed addenda polyoxometalate oxidation systems. Neumann studied vanadium containing mixed addenda Keggin polyoxometalates of the general formula $XM_{10}V_2O_{40}$ (X = P or Si; M = Mo or W) as catalysts for the oxidation of benzylic carbons in alkylaromatic compounds by H_2O_2 [154,155]. Comparison of mixed addenda and simple Keggin polyoxometalates indicated that the mixed addenda catalysts show greater activity as follows: $H_5PMo_{10}V_2O_{40}$ (most active) > $H_5PW_{10}V_2O_{40} \gg H_3PMo_{12}O_{40} > H_3PW_{12}O_{40}$ [154]. A series of 18 alkylaromatic compounds were studied and yielded ketone derivatives as the major product; benzyl acetates and carboxylic acids were minor products.

Nine solvents were compared and acetic acid proved the best producing the highest conversion to the desired ketone product [155].

Droege and Finke prepared a novel mixed addenda polyoxometalate of the formula $Si_2W_{18}Nb_6O_{77}^{8-}$, and studied catalytic oxygenation of allylic alcohols to triol products [157]. This paper went further than many by then evaluating the rate law ($-d$[allyl alcohol]/$dt = k$[allyl alcohol]$[H_2O_2]^{\sim 1.4}$ [polyoxometalate precursor] $^{\sim 0.4}$). The kinetic information and other data are consistent with fragmentation of the catalyst precursor [157].

Hou and Hill just reported the first alkoxypolyoxometalates that are not readily hydrolyzed in aqueous media, thus providing entry into polyoxometalates with covalently attached organic (or biological) groups for applications in aqueous phase catalysis and medicine [164]. These complexes of formula $RC(CH_2O)_3P_2W_{15}V_3O_{59}^{6-}$, $R = CH_3$, NO_2, and CH_2OH, prepared in very high yield (>90%) by the stoichiometric condensation of the 1,1,1-tris(hydroxymethyl)-ethane derivatives with ${}^4Q_5H_4P_2W_{15}V_3O_{62}$, where ${}^4Q = (n\text{-}C_4H_9)_4N^+$, in CH_3CN, have halflives of hydrolysis of $\sim 10^3$ h in D_2O with pD = 0 at 100 °C! Several experiments with the thioether mustard gas analog tetrahydrothiophene (THT) demonstrated that these tris capped complexes are capable of catalyzing oxygenation (Eq. (25)) without apparent decomposition (30 turnovers). Comparative kinetics methods gave the following order of reactivity for oxidation of THT by *t*-butylhydroperoxide (TBHP): ${}^4Q_2H_4CH_3(CH_2O)_3P_2W_{15}V_3O_{59}$ (fastest catalyst) > $OV(O\text{-}{}^iPr)_3$ (a monomeric V(V) model for breakdown of $CH_3(CH_2O)_3P_2W_{15}V_3O_{59}^{6-}$ during turnover) > $(n\text{-}Bu_4N)_2WO_4$ (a monomeric W(VI) model) > ${}^4Q_5H_4V_3P_2W_{15}O_{62}$ (the parent complex) > ${}^4Q_5HCH_3(CH_2O)_3P_2W_{15}V_3O_{59}$ > ${}^4Q_6P_2W_{18}O_{62}$ > no catalyst (slowest). The evaluated rate law and activation energy are $+d[THTO]/dt = k[THT][TBHP][CH_3(CH_2O)_3P_2W_{15}V_3O_{59}^{6-}]^2$, and $E_a = 10.1$ kcal mol^{-1} [164].



(25)

A range of heteropolyoxoanions catalyze the oxidation of thioether analogs of mustard (HD) to the corresponding sulfoxides by *t*-butylhydroperoxide (TBHP) rapidly at 25 °C, with selectivities as high as any seen in the literature for thioether oxidations. The strongly acidic complexes $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ function primarily as acid catalysts for thioether oxidation by TBHP, producing sulfoxide with 98–99% selectivities (1–3% sulfone present) at modest conversions. Gall and Hill just reported the oxidation of THT and other thioethers by TBHP catalyzed by vanadium-substituted heteropoly acids, including hydrated $H_5PMo_{10}V_2O_{40}$, that proceeds in >99.9% selectivity [165]. No sulfone ($THTO_2$) is detectable at the limits of several methods (1 part in 10^5). These oxidations proceed by a novel mechanism for metal catalyzed peroxide oxidations that accounts for this very high selectivity, namely Eq. (8) (Fig. 3) followed by Eq. (9) (Fig. 3). The direct oxidation of THT by $H_5PMo_{10}V_2O_{40}$ has been investigated as closely as any reaction in the literature catalyzed by mixed addenda polyoxometalates. While readers are referred to the original paper for all the details, this reaction is inhibited by water and exhibits the rate law $-d[R_2S]/dt = k[THT][H_5PMo_{10}V_2O_{40}][H_2O]^{-1}$. In the absence of water, the rate becomes independent of THT substrate ($-d[R_2S]/dt = k[H_5PMo_{10}V_2O_{40}]$) and dehydration of the polyoxometalate may be rate limiting. The complete rate law is given in Eq. (26) and all the data, including the activation parameters ($\Delta H\ddagger = 8.06 \pm 0.64$ kcal mol^{-1} and $\Delta S\ddagger = -29.7 \pm 0.18$ e.u.), are most consistent with rate limiting electron transfer between thioether and $H_5PMo_{10}V_2O_{40}$ [165].

$$\frac{-d[R_2S]}{dt} = \frac{k_1k_2[R_2S][H_5PMo_{10}V_2O_{40}]_{total}}{k_1 + k_{-1}[H_2O] + k_2[R_2S]} \tag{26}$$

3.1.2. *Acid catalyzed reactions*

While many acid forms of polyoxometalates (protons as gegenions) exist, most belong to the common Keggin and Wells–Dawson structural classes and hence the very common term "heteropolyacids". This term is so common it is often inappropriately used by noncognoscenti to refer to all polyoxometalates. The word heteropolyacids is partially a misnomer which leads to a key issue. The protons do not reside directly on the heteropolyacid oxygens as they do on some polyoxometalates (cf. $H_3V_{10}O_{28}^{3-}$) [178] but rather on the water molecules of hydration that accompany most heteropolyacids and all soluble examples of this particular class of polyoxometalates. In other words, heteropolyacids, to a good approximation, are hydronium cations stabilized by heteropolyanions. Upon dehydration, the ease of which varies considerably with the particular complex, the protons move to the polyoxoanion oxygens. As the negative charge density on most polyoxometalates including the Keggin and Wells–Dawson complexes is even below that of the conjugate bases of the strongest conventional acids such as ClO_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, etc., it is not surprising that the dehydrated heteropolyacids are often superacids. It is noted for completeness that mixed acid salts (proton plus other cation(s)) of heteropoly compounds can sometimes be superacids [179].

Heteropolyacids have been shown to catalyze many acid-catalyzed reactions such as ester exchange [167] and cyclotrimerization of aliphatic aldehydes [172,173]. For a fairly complete tabulation of these reactions one is referred to recent reviews by Misono [22,46]. Again, as these reactions entail a modest involvement of the polyoxoanions mechanistically and they have been adequately addressed in the above reviews, we will not reiterate this chemistry in detail one more time here. Heteropolyacids containing tungsten have been shown to be more stable than heteropolyacids containing molybdenum, consistent with the general lower lability of polyoxotungstates than the corresponding polyoxomolybdates. Misono and coworkers used polyoxotungstate derivatives to evaluate the effect of different central heteroatoms on the catalytic activity in homogeneous reactions [167]. The order $H_3PW_{12}O_{40}$ (most active) > $H_4SiW_{12}O_{40}$ ~ $H_4GeW_{12}O_{40}$ > $H_5BW_{12}O_{40}$ > $H_6CoW_{12}O_{40}$ (least active) is consistent with the acidities of these complexes, which in turn correlates with the trend in negative charge densities ($H_3PW_{12}O_{40}$ most acidic and $H_6CoW_{12}O_{40}$ least acidic) [167]. Sao and coworkers have examined the cyclotrimerization of aldehydes producing 2,4,6-trialkyl-1,3,5-trioxanes in high yields [172]. In these high yield reactions, the reaction mixture spontaneously separates into two liquid phases, a product phase and a catalyst phase [172]. This is phenomenologically similar to the commercial process for THF polymerization catalyzed by heteropolyacids in which a degree of molecular weight selectivity can be obtained by selective precipitation of product polymer in a particular molecular weight range [22,180].

3.1.3. Multiple function reactions

The robust nature of many families of polyoxometalates coupled with the alterability of their properties suggests new reaction modes and reaction engineering possibilities. For example, a single polyoxometalate might be formulated to catalyze more than one reaction in a multireaction process or technology. Each reaction could be conducted separately in space (different reactors) and/or time (different conditions). A complex problem of considerable current technological, societal and economic significance, the bleaching and processing of wood pulp for paper manufacture, led to an initial attempt at using a polyoxometalate to catalyze multiple functions. This work is a collaboration between Ira Weinstock, Rajai Atalla, and co-workers of the U.S. Forest Products Laboratory, our laboratory at Emory University, the University of Wisconsin Department of Chemical Engineering, and companies in the pulp and paper industry.

First, the prototype process, depicted at the top of Fig. 4, involves bleaching of pulp without the use of chlorinated oxidants of any kind, obviating the production of dioxins and other ecologically unacceptable chlorinated organics. Second, the most economically and environmentally desirable oxidant (O_2) and solvent (H_2O) are used. Third, no organic effluent of any kind is released into the environment ("mill closure" is achieved), and fourth, several engineering features including energy consumption are attractive. The first patents and papers on this chemistry have just appeared [181–183].

The two steps that add up to the net reaction at the top of Fig. 4 are shown in a cycle at the bottom of Fig. 4. First, the oxidized polyoxometalate selectively oxidizes the lignin ($LigH_2$ in Fig. 4) to fragments (Lig in Fig. 4) and is stoichiometrically reduced. The polyoxometalate properties pertinent to the redox reaction (potentials, etc.) can be tuned by the composition, molecular charge, protonation state and so on, so that this bleaching step is highly selective. That is, the lignin is extensively oxidized and oxidatively depolymerized while the cellulose is hardly modified at all. The selective removal of lignin without damage to the cellulose is the general goal in pulp bleaching; it is the cellulose that imparts the strength and substance to the main pulp product, paper. The redox and reactivity tuning of polyoxometalates has led to some complexes, including $SiW_{11}VO_{40}^{5-}$, that exceed the industrial bleaching standard for chlorine. The second step involves complete conversion of the partly

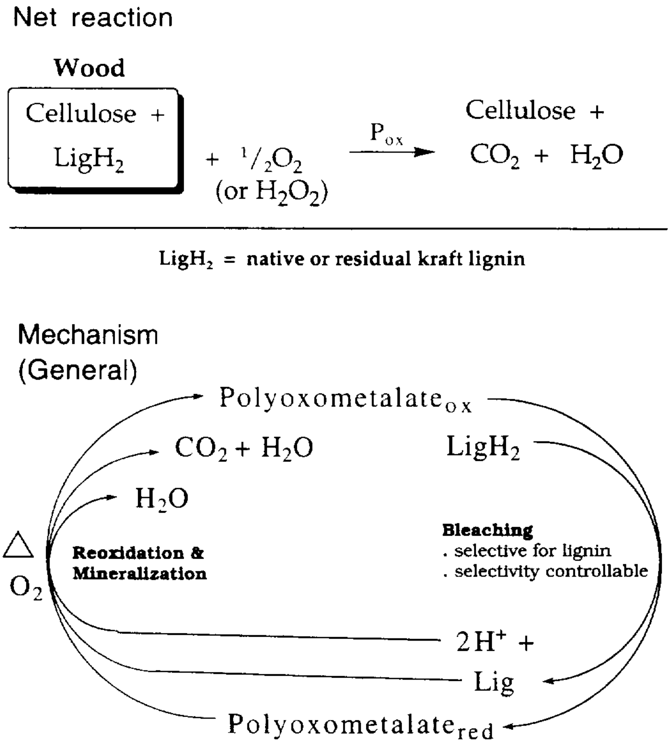


Fig. 4. Top: net reaction for the selective aerobic oxidative delignification of wood pulp with no organic waste catalyzed by polyoxometalates (P_{ox}). Bottom: two component processes that add to the net one. The reaction on the right is selective bleaching of the pulp (oxidation of lignin only and reduction of polyoxometalate) and takes place in one reactor. The reaction on the left is aerobic mineralization (conversion to CO_2 and H_2O) of partially oxidized lignin effluents catalyzed by the polyoxometalate and takes place in a second reactor at high temperature.

oxidized lignin (Lig in Fig. 4) to CO_2 and H_2O, a process catalyzed by the polyoxometalate, in a separate reactor at high temperature. The polyoxometalate is one type of homogeneous catalyst that can not only function in two reaction conditions as different as those in the bleaching and mineralization steps but also withstand oxidative degradation under conditions in which nearly all organic compounds would be degraded (the mineralization reaction conditions of the second step).

Given the number of other complicated multi-reaction processes and the growing environmental concerns on the part of scientists, administrators, legislators and others, the landscape in principle is extensive for development of other applications that require polyoxometalates to fulfil more than one specific molecular chemical function.

3.2. *Mechanistic overview of reactions*

The dominant mechanism in homogeneous oxidations catalyzed by mixed addenda polyanions involves Eqs. (8) and (9) in Fig. 3. While this type of mechanism is highly unusual if not unprecedented for metal catalyzed oxidations by peroxides, it is operable in the one case summarized by the rate law in Eq. (26). In contrast, the common mechanism for homogeneous metal catalyzed peroxide epoxidations, and other oxidations, involving heterolytic activation of the peroxide and no reduction of the metal complex, a mechanism not shown in Fig. 3, is definitely operable for only one polyoxometalate catalyzed reaction thus far, that illustrated in Eq. (25). It is noted that other systems including the Ishii–Venturello chemistry (Ishii precursors $= PW_{12}O_{40}^{3-}$, for example), as outlined above, involve ready polyoxometalate breakdown and are not accurately termed "catalysis by polyoxometalates". When more informative mechanistic studies are conducted on a variety of other H_2O_2 or ROOH based oxidations catalyzed by polyoxometalates, mechanisms involving heterolytic activation of peroxides by intact or largely intact polyoxometalates may become common.

For polyoxometalate facilitated O_2 oxidations not involving aldehydes, carboxylic acids or other species that can form electrophilic peracids or peracid-like intermediates in situ, the mechanisms are poorly understood at best. Kinetics investigations of a number of kinds on systems with carefully characterized polyoxometalate catalysts need to be conducted to sort out to what extent multiple mechanisms, autoxidation components, and carbocation intermediates (from in situ radical oxidation) are operable. While we [10,184–186] and others [187,188] have documented and examined the first chemistry involving radicals and polyoxometalates, more thermodynamic and kinetic information is needed here for these common interactions to be predicted and to be of predictive value in catalytic processes. While our group has documented and investigated to a limited extent the involvement of carbocations and carbanions in polyoxometalate catalyzed oxidations [10,184–186], less is known about these interactions/reactions than those involving radicals and polyoxometalates. As carbocations and carbanions clearly can affect the product determining step in catalytic transformations, their chemistry with polyoxometalates should be investigated quantitatively. This can be done by generating these intermediates via authentic precursors and chemistry in the presence of a range of polyoxometalates varying in redox potential.

A key point often overlooked in studies of metal mediated oxidations of organic substrates by O_2 is that autoxidation can sometimes produce particular organic oxidation products with surprisingly high selectivities, leading to an erroneous conclusion that other generally more selective processes such as oxygenation (Eq. (2)) are operable. One case in point is the O_2 oxidation of some dienes, including olefinic alcohol acetates "catalyzed" by $[Fe_3O(OCOR)_6L_3]^+$ [189]. Subsequent research indicated that this chemistry was effectively a conventional radical chain oxidation; the high selectivity was principally a fortuitous consequence of the reaction conditions and particular substrates used [190].

4. Catalyst combinations

Reactions catalyzed by a combination of compounds or composite compounds that include polyoxometalates are given in Table 4. Soviet investigators, and particu-

Reactions catalyzed by combinations of compounds that include polyoxometalates

Catalyst[a]	Oxidant or reductant[b]	Solvent[c]	Substrate	Products[d]	Comments	Reference
1. Oxidation reactions						
$^4Q_5Na_3[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$, M = Ir or Rh	O_2[e]	CH_2Cl_2[f]	alkene	allylic ketone allylic alcohol, epoxide	38 °C	[142]
$^4Q_5Na_3[(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}]$	O_2	CH_2Cl_2	alkene	allylic ketone allylic alcohol, epoxide	38 °C	[142]
$Na_yH_{(3+x-y)}PMo_{(12-x)}V_xO_{40}$ palladium	O_2[g]	H_2O	ethylene	acetaldehyde	115 °C, N_2 NaCl	[139,140]
$Na_yH_{(3+x-y)}PMo_{(12-x)}V_xO_{40}$ palladium	O_2[g]	H_2O	CO	CO_2	115 °C, N_2 NaCl	[139]
2. Reduction reactions						
$Li_4SiM_{12}O_{40}$ and $RhCl(PPh_3)_3$, M = W or Mo	H_2	C_6H_6/EtOH	alkene	alkane	30 °C	[191]
$^4Q_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$	H_2	CH_3COCH_3	alkene	alkane	22 °C	[192]
3. Other reactions						
$PdCl_2$ and $H_3PW_{12}O_{40}$, $PdCl_2$ and $H_4SiW_{12}O_{40}$ or $PdCl_2$ and $H_4PVMo_{11}O_{40}$	CO	DME	nitrobenzene methanol	methyl *N*-phenylcarbamate	170 °C	[193]
$PdCl_2$ and $X_3PMo_{12}O_{40}$[h] or $PdCl_2$ and $X_4SiMo_{12}O_{40}$, X = H or Li	CO	DME[i]	nitrobenzene methanol	methyl *N*-phenylcarbamate	170 °C	[193]
$PdCl_2$ or $H_3PMo_{12}O_{40}$	CO	DME	nitrobenzene methanol	no rxn	170 °C	[193]

[a] $^4Q = (n\text{-}C_4H_9)_4N^+$; COD = cyclooctadiene. [b] Either the oxidant or the reductant used in the reaction is listed in this column. [c] DME = dimethoxyethane. [d] no rxn = no reaction was observed. [e] Other oxidants ($H_2 + O_2$ or H_2O_2) were examined with $^4Q_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ catalyst and found to produce the same products as O_2. [f] The solvent effect was evaluated for $^4Q_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$ catalyst. Alkene reacted in CH_2Cl_2, 1,2-$C_2H_4Cl_2$, $(CH_3)_2CO$ or CH_3CN, but no reaction was observed in DMSO or $CH_3CON(CH_3)_2$. [g] Air reactor used to reoxidize the reduced vanadium. [h] $Pd(OAc)_2$, $PdSO_4$, $Pd(NO_3)_2$, Pd/C and Pd black were also examined with $H_3PMo_{12}O_{40}$ and no $PhNO_2$ conversion was observed. $Pd(NH_3)_2Cl_2$, $Pd(PPh_3)_2Cl_2$, $RhCl_3$ and $RuCl_3$ were also examined with $H_3PMo_{12}O_{40}$ and $PhNO_2$ conversion was observed. [i] The solvent effect was evaluated for the $PdCl_2$ and $H_3PMo_{12}O_{40}$ system. $PhNO_2$ conversion was observed when the following solvents were used: acetone, 2-butanone, 2-pentanone, methyl isopropyl ketone, 2-hexanone, cyclohexanone, THF, DME, diisopropyl ether, methyl *n*-caproate, DMF, *n*-octane, 1,2 dichloroethane and methanol. $PhNO_2$ conversion was not observed when DMSO was used as solvent.

larly the Novosibirsk group of Matveev, Kozhevnikov and co-workers, are largely responsible for the early development of two component (nonbonded) catalytic systems, with heteropoly acid/M, M = Pd or Pt (see reviews of this early research in Refs. [17] and [18]). A considerable number of reactions of this type were reported in this early literature and in nearly all cases it is the Pd (Pt) and not the polyoxometalate that directly interacts with and oxidizes the substrate. The Novosibirsk group also gets credit for some early seminal discoveries in the application of polyoxometalates in homogeneous catalysis, including the fact that vanadium(V) in Keggin vanadium-substituted polymolybdophosphates is a dioxygen-regenerable oxidant that essentially can take the place of copper chlorides in Wacker chemistry.

Some of the most informative and valuable recent research in homogeneous catalysis by polyoxometalates has been olefin oxidation systems developed by the Grate group at Catalytica, Inc. [137,139–141]. This research builds on the Novosibirsk system for olefin oxidation, typically ~2 mM $PdSO_4$, ~0.2 M mixture of $H_{(3+x)}PMo_{(12-x)}V_xO_{40}$, that was in turn related to the older Wacker technology. Extensive kinetics and optimization studies by Grate and co-workers led to an improved $Pd/PMo_{(12-x)}V_xO_{40}^{(3+x)-}$ system that overcomes three limitations of the Novosibirsk system with respect to commercial viability: (1) poor Pd(II) catalyst stability, (2) an ethylene reaction rate ca. an order of magnitude too slow, and (3) an oxygen reaction rate ca. an order of magnitude too slow [140]. Catalytica's system for ethylene oxidation is typically aqueous ~0.30 M in polymolybdophosphate, ~0.1 mM in Pd(II), and ~5–25 mM in Cl^-. The concentrations of the latter two species are two orders of magnitude lower than those in the Wacker system. In the Wacker, Novosibirsk, and Catalytica systems, it is the Pd(II) which actually oxidizes olefinic substrate; the polyoxometalate efficiently reoxidizes the Pd(0) to Pd(II) in the latter two systems. Grate and co-workers evaluated the kinetics of their systems over a wide range of conditions. The speciation thermodynamics of Pd as a function of pH and chloride in the catalytically relevant regime are complex and make for complicated rate laws. For details of the rate behavior and optimization of chemistry and engineering, one is refereed to the original articles [139,140].

An important feature of this work involved a collaboration between the Catalytica group and L. Pettersson and co-workers in Sweden, some of the foremost experts in the area of polyoxometalate speciation thermodynamics. Two recent papers describe application of NMR, potentiometric and other methods to the quantitative delineation of vanadium(V)-substituted polymolybdophosphate speciation under conditions of relevance to the Catalytica research [136,138]. See also a recent paper by Pettersson and Grate on thermodynamic speciation of the aqueous vanadophosphate system [137].

4.1. Oxidation reactions

Mizuno, Lyon and Finke reported the oxidation of cyclohexene by molecular oxygen in the presence of three polyoxoanion-supported transition-metal complexes, $^4Q_5Na_3(1{,}5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}$, M = Ir or Rh and $^4Q_{2.5}Na_{2.5}(C_6H_6)Ru\cdot P_2W_{15}Nb_3O_{62}$ [142]. They report a 4.2% conversion of cyclohexene to cyclohexenone, cyclohexenol, and cyclohexene oxide in selectivities of 62%, 32%, and 5%, respectively. The rate is solvent dependent, decreasing as follows: dichloromethane > 1,2-dichloroethane > acetone > acetonitrile ≫ *N,N*-dimethylacetamide ~ dimethylsulfoxide [142]. Some preliminary kinetics were presented but more points were required for significant interpretation as the rate law exhibits saturation kinetics. While the title and thrust of this paper is that the complexes are catalysts, the product distributions are typically those seen in radical chain O_2 oxidations. The authors realize that this and the kinetics are not inconsistent with the likely situation that these complexes are functioning primarily to initiate autoxidation and not actually catalyzing "oxygenation", to use the words of the authors. The oxidation processes associated with the meticulously characterized polyoxometalate-supported organometallic species by this group warrant an in-depth examination, and we understand that the needed mechanistic studies are in fact nearing completion [194].

4.2. *Reduction reactions*

Finke and coworkers reported the synthesis, characterization, catalytic alkene hydrogenation activity, kinetics, and mechanistic studies on the polyoxometalate-supported organometallic complex $^4Q_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$ [192,195]. As polydisperse catalytically active Ir(0) nanoclusters are produced in these reactions, this chemistry is discussed below (Section 5, Related literature studies).

4.3. *Other reactions*

Izumi and coworkers reported the high yield synthesis of methyl *N*-phenyl carbamate from reductive carbonylation catalyzed by a mixture of $PdCl_2$ and Keggin type heteropolyanions containing Mo or V as addenda atoms; Eq. (27) and Table 4 [193]. Neither $PdCl_2$ nor the polyoxometalate alone is catalytically effective. The reaction rate, calculated from $PhNO_2$ conversion data based on the empirical zero-order dependence of the conversion on reaction time, increased in proportion to both CO pressure and Pd concentration but showed a 0.43-order dependence on the concentration of $PhNO_2$. The apparent activation energy was estimated to be 38 kJ mol^{-1}. It is hard to know exactly what these kinetics mean in this complex system given the limited data but the authors rightly conclude that the mechanism of this potentially useful reaction is quite unclear [193].

$$PhNO_2 + 3CO + CH_3OH \rightarrow PhNHCO_2CH_3 + 2CO_2 \tag{27}$$

5. Related literature studies

Other studies, while not rigorously falling under the purview of this article on homogeneous catalysis by polyoxometalates, are related phenomenologically and intellectually to this subject and thus we would like to address them. The first are the recent studies by Finke and coworkers on the decomposition of electron-rich-polyoxometalate-supported Ir complexes, and principally

${}^4Q_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$, to form polyoxometalate-stabilized Ir(0) nanoclusters during alkene hydrogenation. The term nanoclusters was used as the clusters are in this size regime (e.g. 30 ± 4 Å and 20 ± 4 Å depending on the conditions of preparation). While these Ir(0) nanoclusters are polydisperse and as such would not be included in this review on catalysis by discrete molecules (monodisperse systems), this work is of sufficient interest to mention here. Initially, these authors argued that alkene hydrogenation was being catalyzed by the discrete well-characterized molecule, ${}^4Q_5Na_3[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]$ [192,195]. The authors initially and reasonably ruled out a $[Ir(0)_n]$ colloid based on three observations: first, evaporation of the catalyst solution to dryness and redissolution produced no visible Ir(0) colloid; second, molecular weight measurements were consistent with monomer; and third, the reproducibility of both the hydrogenation curve and the reaction rate was high (±15%) [195]. Subsequent work by these investigators, however, including transmission electron micrographs of the samples after reaction, provided compelling evidence that Ir(0) colloids with unusually uniform particle sizes are in fact formed during alkene hydrogenation and that these colloidal nanoclusters are the catalytically competent species [196]. The spatial uniformity and stability of these clusters are of interest and these systems provide as good a vehicle as any to address the structural and dynamic features of the molecule–colloid boundary. For descriptions of the thorough characterization of these Ir(0) nanoclusters and their chemistry, one is referred to the appropriate papers [197,198].

The second study, that of Day, Klemperer and co-workers, is included here even though it strictly doesn't involve either an early-transition-metal polyoxometalate or catalysis. These investigators conducted a stoichiometric oxidation of an Ir complex with two ligands: 1,5-cylooctadiene, the substrate, and cyclotriphosphate, a polydentate ligand structurally analogous to the surfaces of some early-transition-metal polyoxometalates. $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ reacts with 1/2 O_2 to form an oxometallocyclobutane, $[(C_8H_{12}O)Ir(P_3O_9)]^{2-}$, which rearranges to π-allyl hydroxy complex, $[(C_8H_{11}OH)Ir(P_3O_9)]^{2-}$. All three complexes were characterized by X-ray crystallography [199]. While it has been intellectually argued and physically demonstrated that metal complexes isolated from metal-complex-catalyzed reactions usually do not lie along the principal catalysis reaction coordinate and are hence marginally relevant to catalysis [200,201], the extensive work of Burgi and Dunitz [202] argues effectively that a series of static structures map out a reaction surface approximating a reaction coordinate. This initial elegant effort of Day and Klemperer provides structural information that is probably of some predictive value. These investigators are interested in making this system catalytic.

6. Ion pairing in polyoxometalates

One phenomenon that requires significant research is ion pairing in polyoxometalates and, more generally, ionic interactions of these compounds in solution, where nearly all homogeneous catalysis takes place. The strength, number, lifetimes and other features of cation–polyanion and to a lesser extent cation–cation and polyanion–polyanion interactions that affect, to varying degrees, every molecular attribute of polyoxometalates involved in their solution chemistry and catalysis must be more thoroughly investigated. These attributes include effective charge, ability to form hydrogen and ionic bonds, ground state redox potential and, less importantly, effective size (hydrodynamic radius) and shape. Only limited information is available on polyoxometalate ion pairing interactions in both aqueous and nonaqueous solvents. Some early published work provides quantitative and insightful thermodynamic and kinetic information on ion pairing in $V_{10}O_{28}^{6-}$ and some Keggin-derived complexes in water [203–205]. Unfortunately, this work was terminated before the versatility and value of polyoxometalates in catalysis and other areas of science and technology was fully appreciated. Static structural effects of ion binding in $Nb_2W_4O_{19}^{4-}$ [206,207] and $V_{10}O_{28}^{6-}$ (careful X-ray diffraction, vapor pressure osmometry and multinuclear solution NMR) [178] have been documented by Day and Klemperer and co-workers. Hill and co-workers have documented ion pairing and solvation effects on the electronic absorption and photochemical action spectra of polyoxometalates [208–210] and protonation state effects on the dynamic behavior (rates and selectivities of products) in photocatalytic alkane functionalization [185]. Finke and co-workers reported the stepwise deprotonation of $H_3SiW_9V_3O_{40}^{4-}$ and $H_4P_2W_{15}V_3O_{62}^{5-}$ in organic solvents and garnered qualitative information about proton mobility in these dissolved complexes from documenting the effects of protonation and the presence of water, pyridine and pyridinum on the ^{29}Si, ^{31}P, ^{51}V and ^{183}W NMR spectra of these complexes [211]. This group also addressed the combinatorial possibilities associated with multiple cations and highly charged polyanions in a footnote to one paper [212]. The only recent study that addresses dynamic ion pairing effects in a semiquantitative manner involves examination of the electron exchange rates between Keggin complexes in water as a function of ionic strength [213]. A surprisingly good fit to an equation derived from Debye–Huckel theory was given. Future work must seek to document and understand ionic effects in polyoxometalate complexes under conditions of homogeneous catalysis. The strengths and lifetimes of such interactions and their effects on association of substrates, dissociation of products and other phenomena relevant to catalysis must be assessed. This will require simultaneous application of definitive probes of solution structure and detailed kinetics studies.

7. Outlook

Considerable research, most of quite recent vintage, on homogeneous catalysis by polyoxometalates, coupled with the continuing development of commercially viable systems buttress the points made at the outset: polyoxometalates are an extraordinarily versatile class of complexes with potential catalytic application for a variety of attractive processes. These include O_2 and H_2O_2-based oxidations and processes that take place under environmentally benign conditions.

Polyoxometalates, as nanoscopic clusters, offer properties not seen in solid heterogeneous catalysts nor in soluble monomeric homogeneous catalysts. Their intrinsic compositions enable many to exhibit the stability advantages of heterogeneous catalysts with the tunability and selectivity advantages of homogeneous catalysts.

To temper the obvious promise of polyoxometalates, we must realize that considerable fundamental work, much of it at a more definitive level of molecular sophistication than most reported so far, is needed if this area is to advance to realize its promise.

The knowledge we will garner from such studies will give us more predictive power in designing effective and successful homogeneous polyoxometalate-based catalytic technology of value in synthesis, materials science, and possibly medicine.

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