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Another Example of the Instability of a Keggin-Type Heteropolyanion in the Presence of Aqueous Hydrogen Peroxide: From $[AsW_{12}O_{40}]^{3-}$ to Low-Nuclearity Oxoperoxotungstates – Crystal Structure of $[(n\text{Hex})_4N]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$

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The Keggin dodecatungstoarsenato anion of $HNa_2[AsW_{12}O_{40}]$ is inherently unstable in aqueous hydrogen peroxide and is mainly degraded to $[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$, $[HAsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ and $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$. These anions were isolated as salts and identified by elemental and spectroscopic analyses. The salt with the formula $[(nC_6H_{13})_4]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ was obtained from the reaction of tungstic acid, "H_2WO_4" (or $HNa_2[AsW_{12}O_{40}]\cdot nH_2O$), with aqueous hydrogen peroxide, $HNa_2[AsO_4]\cdot 7H_2O$ and $[(nC_6H_{13})_4N]Cl$. The structure was refined with $R_1 = 0.058$ and $wR_2 = 0.067$ [monoclinic $C2$ (no. 5); $a = 20.516(6)$ Å, $b = 15.923(4)$ Å, $c = 14.902(2)$ Å, $\beta = 91.64(1)°$, $Z = 2$]. The vibrational spectra (IR and Raman) suggest that the overall structure is maintained in organic solvents. The close relation between the phosphate- and arsenate-based complexes indicates that fluxional behaviour may exist for all these di- and tetranuclear complexes. Fluxionality may play a key role in the transfer of active oxygen (from peroxo groups) to organic substrates via $\{WO(O_2)_2\}$ units. It is shown that the heteroligand $[XO_p]^{n-}$ (X = As, HAs, MeAs, P, HP, etc.) has a marked effect on the stoichiometric and regioselective epoxidation of (*R*)-(+)-limonene to 1,2-epoxide at ambient temperature, for a given pH of the aqueous phase. The oxodiperoxo complexes can be used to carry out epoxidation stoichiometrically and regioselectively with (*R*)-(+)-limonene, but can also be employed in a catalytic process in a two-phase mixture at room temperature.

Introduction

Heteroligand peroxo-transition-metal complexes possess coordination spheres composed of one to three peroxo groups, and one or more monodentate or polydentate ligands. The stability of the peroxo complex can be enhanced and the reactivity of the coordinated peroxo group changed by specific heteroligand combinations.[1–7] A novel class of heteropolyoxoperoxometalate complexes has attracted attention.[1–14] Representatives of this class are the tetranuclear complexes $Q_3[PO_4\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (denoted "PM_4"; compound **1**: M = Mo and Q^+ = amino-2 pyridinium[8] or $Q^+ = [(n\text{Hex})_4N]^+$;[9] compound **2**: M = W and $Q^+ = [(n\text{Hex})_4N]^+$[10–12]) and the parent dinuclear complexes $[(nBu)_4N]_2[REO_3\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]\cdot xH_2O$ (compound **3**: R = OH and E = P[13] with $x = 0$; compound **4**: R = OH and E = As[14] with $x = 0$; compound **5**: R = CH_3 and E = As[14] with $x = 1$).

The dimeric moiety $[M_2O_2(\mu\text{-}O_2)_2(O_2)_2]$ is a building block for these five anions. To the best of our knowledge, it has not been observed in peroxotungsten complexes with oxo,[15] oxalate[16] and carbonate[17] or in oxoperoxomolybdates[18,19] with molybdate as assembling ligands, $[\{MoO(O_2)_2\}_2(\mu\text{-}MoO_4)\{\mu\text{-}O\}]^{4-}$ and $[\{\{MoO(O_2)_2\}_2(\mu\text{-}O)\}_2(\mu_4\text{-}MoO_4)]^{6-}$. Complexes with[20] and without[20,21] the dimeric moiety $[M_2O_2(\mu\text{-}O_2)_2(O_2)_2]$ have been synthesised with sulfate as the assembling ligand.

On the one hand, it was shown that both the "$H_3[PW_{12}O_{40}]\cdot nH_2O/(H_2O_2/H_2O)$" and the "$H_2WO_4/H_3PO_4/(H_2O_2/H_2O)$" systems involve common species, $[PW_xO_y]^{w-}$, x = 1–4. The Keggin-type heteropolyoxometalate (POM) is degraded by H_2O_2 to form a variety of phosphatooxoperoxo complexes. These, along with other pure oxoperoxotungstates,[13,22,23] for example $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$, have been characterised by IR, Raman, ^{31}P and ^{183}W NMR spectroscopy. In contrast with $H_4[SiW_{12}O_{40}]\cdot nH_2O$, more drastic conditions (70% H_2O_2 in water) have to be used to degrade the Keggin-type polyanionic structure.[23] On the other hand, a new lacunary heteropolyoxotetraperoxotungstate, related to the Keggin structure

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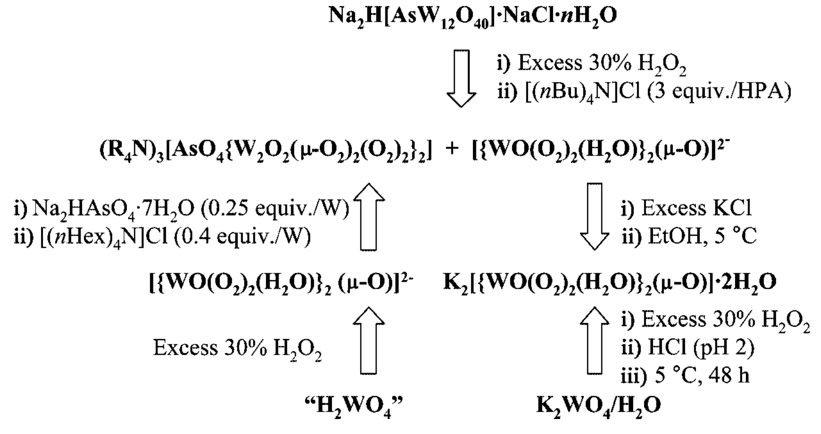
$[(Co^{II}O_4)W_{11}O_{31}(O_2)_4]^{10-}$, has been characterised by single-crystal X-ray diffraction.[24] The authors underlined that the different reactivities of lacunary and saturated Keggin complexes (i.e. $[PM_{12}O_{40}]^{3-}$ where M = Mo or W) towards aqueous H_2O_2 may be related to the longer M=O bonds of the terminal oxygen atoms of *cis*-$W(O)_2$ groups around the vacancy that lead to *cis*-$W(O)(O_2)$. The conversion of $H_3[PM_{12}O_{40}]\cdot nH_2O$ in the presence of hydrogen peroxide should also require the intervention of lacunary precursors, but in equilibrium with $\{MO_2(OH)\}^+$ or $\{MO_2\}^{2+}$ species, which are converted to $\{MO(O_2)_2(H_2O)_2\}$ moieties.[6,13,25] Recent review articles focus on H_2O_2-based epoxidation catalysed by lacunary polyoxometalates,[7] e.g. $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$. The nonlacunary heteropolyoxoperoxometalates $[PTiW_{11}O_{39}(O_2)]^{5-}$ and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ have also been reported.[26,27] In these compounds, the peroxo ligands are probably bonded to the Ti atom (statistical disorder makes it impossible to locate the Ti atoms and the peroxo ligands). These substituted polyoxometalates are moderately active for olefin epoxidation with the use of 30% H_2O_2 (O_{peroxo}/catalyst = 1200:2 mol/mol). It is inferred that there is no degradation of the Keggin-structured framework at 50 °C over 24 h,[27] although synergy may exist between the tungsten and titanium centres. The retention of the Keggin unit of this Ti–POM was reinvestigated,[28] but in some systems the isolable species are often not those that lie along the principal reaction coordinates for the catalysis.[6,25]

Although it was formerly accepted that the O–O bond lengths are fairly constant and do not depend on the nature of the metal ligands, we were interested in a systematic study of the heteroligand effect. This is of major importance for catalysis in homogeneous[6,29] or two-phase-medium[6,9,13,22,23,30,31] conditions, for grafting onto (or inserting in) polymeric supports[6,30,32–38] or for the comprehensive study of the synthesis of transition-metal-containing mesostructured materials from peroxo species.[39,40] We report here the synthesis and structural characterisation of $[(nHex)_4N]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (**6**). Salts of the anion have been prepared by several groups;[11–12,41–43] despite many attempts to show that **1**, **2** and **6** are isomorphous, it was previously difficult to isolate single crystals of **6** suitable for X-ray measurements. The profiles of the Raman and infrared spectra of **6** are compared with those of tetra-*n*-butylammonium (μ-hydrogenoarsenato)bis(μ-peroxo)bis(oxoperoxotungstate)(2–) (**4**)[14] and with those of the methylarsenato analogue (**5**).[14] Moreover, it is shown that the interaction of excess H_2O_2 (30%) with an aqueous solution of $[AsW_{12}O_{40}]^{3-}$ leads to the degradation of the Keggin unit and to the formation of a less-condensed oxoperoxo species in the same way as $H_3[PW_{12}O_{40}]\cdot nH_2O$ in the presence of H_2O_2. These complexes are active oxygen-to-olefin transfer agents at room temperature and are active catalysts in the oxidation of model organic substrates using 30% H_2O_2 in water in a two-phase medium.

Results and Discussion

Syntheses of 6: Peroxide-Mediated Decomposition of $[AsW_{12}O_{40}]^{3-}$ or Reaction of H_2O_2 with Tungstic Acid in the Presence of Arsenate

The synthesis of $[(nHex)_4N]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (**6**) from "H_2WO_4" is based on methods that generate oxoperoxo species,[44] mainly $[WO(O_2)_2(H_2O)_2]$, $[WO(OH)(O_2)_2]^-$ and $[\{WO(O_2)_2H_2O\}_2(\mu\text{-}O)]^{2-}$ [with peroxide/tungsten(VI) > 2] which are subsequently coordinated by the assembling anion $[AsO_4]^{3-}$. Another procedure can be developed with the use of $Na_2H[AsW_{12}O_{40}]\cdot NaCl\cdot 30H_2O$, which is degraded by excess H_2O_2 (Scheme 1); these results compare well with previously reported data,[22,23] and spectroscopic evidence shows that the "$H_3[PW_{12}O_{40}]\cdot nH_2O/H_2O_2/H_2O$" and "$H_2WO_4/H_3PO_4/H_2O_2/H_2O$" systems give the same oxoperoxo species.[4,6,10,13,22,23] To precipitate one of the anions formed from $[AsW_{12}O_{40}]^{3-}$ and excess H_2O_2, we added tetra-*n*-butylammonium chloride and isolated the complex $[(nBu)_4N]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$, and subsequently added potassium chloride to give $K_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$. Therefore, the appropriate choice of counteranions allowed us to obtain the two oxoperoxo salts selectively (Scheme 1). The products have been fully characterised by an active oxygen assay, elemental analysis and vibrational studies (IR and Raman spectra, vide infra). The isolation of **6** led to structural X-ray data.



Scheme 1. Synthesis of anionic peroxo complexes involving the arsenato ligand (R = *n*Bu or *n*Hex).

Structure of the Tetranuclear Complex $[(n\text{Hex})_4\text{N}]_3[\text{AsO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]$ (6)

The arsenic atom of $[\text{AsO}_4]^{3-}$ and one of the nitrogen atoms, N(2), lie on a binary axis. The neutral moiety, $\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$, and the other nitrogen atom, N(1), are in general positions, while the other two locations are generated by the binary axis.

Single-crystal X-ray analyses show that **1**,[9] **2**[10] and **6** (this work) are isomorphous and are structurally very similar. The anion of **6** (Figure 1) consists of a slightly distorted tetrahedral assembling anion, $[\text{AsO}_4]^{3-}$, and two neutral units, $\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}$, in which the tungsten(VI) atoms are coordinated by seven oxygen atoms in a pentagonal-bipyramidal arrangement (PBPY-7, IUPAC Nomenclature). The four oxygen atoms of the anion are corner sharing with the four different basal planes of the pentagonal bipyramids. Atoms O(3) and O(4) of the arsenate bridge two tungsten atoms within a dinuclear unit. The geometry about the arsenic atom does not deviate significantly from that of a tetrahedral arrangement (Table 1), with a mean bond angle of 109.5°. The As–O bond lengths average 1.66 Å, in agreement with those of **4**, **5**[14] and many tungsten(VI) arsenates containing heteropolyanions, and with values found for arsenates and organoarsenates.[45,46] The tungsten atoms have two differently bound peroxo ligands: one is in the η^2-side-bound configuration, [W(1)–O(11)–O(12) and W(2)–O(21)–O(22)] (Figure 1), and the other is in the μ_2-η^2:η^1 mode (or unsymmetrical bridging). Thus, in **6**, the tungsten atoms are connected in pairs not only by the $[\text{AsO}_4]^{3-}$ group, but also by the unique μ_2-η^2:η^1 peroxo bridges, and the two pentagonal bipyramids associated in this way share one edge of the nonbasal plane, O(13)···O(23). It is important to note that a similar unit exists only in the anion of **1**[9] and **2**[10], and in the dinuclear complexes that have recently been isolated: **3**,[13] **4**,[14] **5**[14] and $[\text{P(C}_6\text{H}_5)_4]_2[(\text{C}_6\text{H}_5)_2\text{SiO}_2\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}]$ (**7**).[39] The least-squares planes for the anion of **6** are such that the pentagonal bipyramids of the oxygen atoms surrounding the two tungsten atoms are almost identical. Each pentagonal girdle is generated by two peroxo groups and one oxygen atom of the arsenate group. A summary of bond lengths and angles of the anion is presented in Table 1. One of the axial positions is occupied by a terminal oxo ligand O^{2-} (W=O: 1.77, 1.70 Å) and the other by an oxygen atom of a bridging unsymmetrical peroxo group with a notably long bond (W–O: 2.42, 2.37 Å), similar to those found for **4**, **5**[14] and **7**.[39] The oxygen atoms that define the equatorial plane are coplanar to within 0.004–0.143 Å. As is the case for octahedral coordination in polyoxometalates, W(1) and W(2) are located outside the mean plane defined by the five equatorial O atoms (0.37 Å and 0.40 Å, respectively). These distances are also found for the other structural units in **3**, **4**, **5** and **7**.[13,14,39] In the η^2-peroxo groups, O(11)–O(12) and O(21)–O(22) are nearly symmetrically coordinated to W(1) and W(2), respectively [W(1)–O(11) and W(1)–O(12) have bond lengths of 1.92 and 1.90 Å, respectively]. The O(11)–O(12) and O(21)–O(22) bond lengths (1.49 and 1.48 Å, respectively) are in the usual range (1.40–1.50 Å),[1–4] and the corresponding three-membered –W–O–O– rings are nearly isosceles. In contrast to these structural data, the bridging peroxo groups μ_2-η^2:η^1 [O(13)–O(14) and O(23)–O(24)] are dissymetrically coordinated to W(1) and W(2), which results in a relatively long W–O bond with the bridging oxygen atoms [W(1)–O(13) and W(2)–O(23) are 2.06 and 2.00 Å, respectively] and a shorter bond with the second oxygen atom (1.93 and 1.90 Å, respectively), similar to those found for the side-bound peroxo group. The OWO angles are unchanged (about 45°), whereas the peroxo bond lengths lie between 1.48 and 1.52 Å. It is well known that the addition of suitable ancillary ligands (hexamethylphosphorotriamide, HMPA,[47] or pyridine *N*-oxide, pyO)[48] to "H_2WO_4" ("$\text{WO}_3\cdot\text{H}_2\text{O}$") or tungsten powder in 30% H_2O_2 in water leads to the formation of well-characterised molecular complexes: $[\text{WO(O}_2)_2\text{L}^1\text{L}^2]$ where L^1 = HMPA, L^2 = H_2O,[47] or $\text{L}_1 = \text{L}_2$ = pyO.[48] The dinuclear anion, $[\{\text{WO(O}_2)_2(\text{H}_2\text{O})\}_2(\mu\text{-O})]^{2-}$, can also be formed at an early stage of the reaction; it seems likely that the anions of **4**, **5** and **6** are obtained by reactions of the molecular complexes

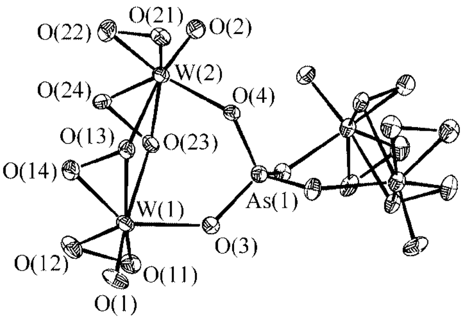


Figure 1. CAMERON view of the anion in **6**, showing the atom-labelling scheme. Atoms are represented by thermal ellipsoids at the 25% level.

Table 1. Selected bond lengths [Å] and angles [°] for $[(n\text{Hex})_4\text{N}]_3[\text{AsO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]$.

W(1)–O(1)	1.773(14)	O(11)–W(1)–O(12)	45.9(6)
W(1)–O(3)	2.011(11)	O(13)–W(1)–O(14)	43.2(5)
W(1)–O(11)	1.917(12)	O(1)–W(1)–O(23)	171.4(6)
W(1)–O(12)	1.903(13)	O(2)–W(2)–O(13)	169.5(5)
W(1)–O(13)	2.059(13)	O(21)–W(2)–O(22)	45.3(6)
W(1)–O(14)	1.928(13)	O(23)–W(2)–O(24)	45.9(5)
W(1)–O(23)	2.415(13)	O(3)–As(1)–O(4)	109.7(5)
W(2)–O(2)	1.700(13)	O(3)′–As(1)–O(4)′	109.7(5)
W(2)–O(4)	2.008(11)	O(4)–As(1)–O(4)′	113.1(8)
W(2)–O(13)	2.366(14)	O(4)–As(1)–O(3)′	107.3(6)
W(2)–O(21)	1.931(11)	O(3)–As(1)–O(4)′	107.3(6)
W(2)–O(22)	1.903(12)	O(3)–As(1)–O(3)′	109.8(9)
W(2)–O(23)	1.994(11)		
W(2)–O(24)	1.899(12)		
As(1)–O(3)	1.667(12)		
As(1)–O(4)	1.650(10)		
O(11)–O(12)	1.489(19)		
O(13)–O(14)	1.472(18)		
O(21)–O(22)	1.48(2)		
O(23)–O(24)	1.521(17)		

($L^1 = L^2 = H_2O$) and/or of dinuclear species with $H_{3-\varepsilon}$-$[AsO_4]^{\varepsilon-}$ species in the same way as that for the phosphatooxoperoxotungstate species for which, according to NMR spectroscopic studies, there are several equilibria.[6,13,22,23]

Infrared and Raman Spectra: Correlation of Vibrational Data with the Structure of Complexes 4, 5 and 6

Attempts to measure the Raman spectra of **1**, **2** and **6** in a benzene solution were unsuccessful,[42] but the solid state and acetonitrile solutions show common features in the 500–1000 cm^{-1} region, which suggests that the structures of the anions of **4**, **5** and **6** are maintained in some organic solvents (here acetonitrile) at room temperature, as proposed in a preliminary structural study.[14] The IR and Raman spectra of **6** are presented in Figure 2 and the attributions of the main infrared and Raman vibrations are given in Table 2.

The infrared and Raman spectra of arsenate-containing complexes show strong bands in the 960–990 cm^{-1} region assigned to $\tilde{\nu}(W{=}O)$ of the terminal oxo group (see Table 2). For tetrahedral XO_4 compounds, four vibrations are expected: $\tilde{\nu}_1(A_1)$, $\tilde{\nu}_2(E)$, $\tilde{\nu}_3(F_2)$ and $\tilde{\nu}_4(F_2)$. With free $[AsO_4]^{3-}$, these maxima are at about 878 ($\tilde{\nu}_3$), 837 ($\tilde{\nu}_1$), 463 ($\tilde{\nu}_4$) and 349 ($\tilde{\nu}_2$) cm^{-1}.[49] Although all of them are Raman-active, only $\tilde{\nu}_3$ and $\tilde{\nu}_4$ are infrared-active for T_d symmetry.[50] We propose that the two strong infrared and Raman bands in the 915–865 cm^{-1} region be attributed to vibrations of the arsenato ligand, i.e. As–O stretches (see Table 2). For "$Na_3[AsW_{12}O_{40}]\cdot nH_2O$"[51] (reformulated as Na_2H-$[AsW_{12}O_{40}]\cdot NaCl\cdot 30H_2O$ – see Experimental Section), an infrared band located at 911 cm^{-1} is attributed to the $\tilde{\nu}_{asym}(As–O)$ vibration.[51] Two infrared bands at 892 and 875 cm^{-1} are also tentatively attributed to the $\tilde{\nu}(AsO_4)$ stretches of the arsenato-containing tetranuclear species.[50]

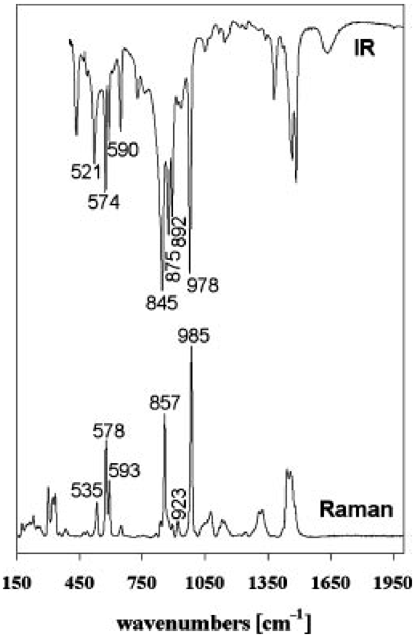


Figure 2. Infrared and Raman spectra of solid samples of $[(nHex)_4N]_3$-$[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (**6**).

The bands at 857–861 cm^{-1} (Raman spectra) and at 843–849 cm^{-1} in the IR spectra are related to the Raman- and infrared-active $\tilde{\nu}(O–O)$ vibrations of the peroxo ligands. These values are in agreement with previously obtained values for tungsten oxoperoxometalates involving other assembling anions and $\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ units,[9,13,14,20,22,23] and also with those from the Raman spectra of many unactivated organic peroxides. We propose to limit the wavenumber region expected for the $\tilde{\nu}(O–O)$ to 830–885 cm^{-1}. Thus, we observed the O–O stretch at 876 cm^{-1} in the spectrum of hydrogen peroxide (30% H_2O_2 in water). Barium peroxide (BaO_2), which is registered in

Table 2. Vibrational wavenumbers [cm^{-1}] of arsenatooxoperoxotungstate complexes **4**, **5** and **6** (main Raman and IR bands).[a]

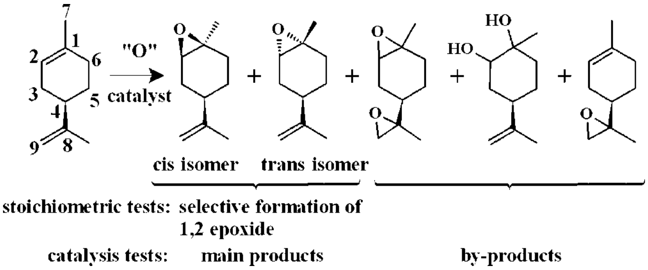
		Compound					
$\tilde{\nu}$ [cm^{-1}]		$(nHex_4N)_3[AsW_4O_{24}]$ **6**		$(nBu_4N)_2[HAsW_2O_{14}]$ **4**		$(nBu_4N)_2[CH_3AsW_2O_{13}]\cdot H_2O$ **5**	
		solid	CH_3CN solution	solid	CH_3CN solution	solid	CH_3CN solution
$\tilde{\nu}(W{=}O)$	IR	978 vs	976 vs	966 vs	970 vs	976 s 964 vs	966 s
	Raman	985(10)	983(10)	978(10)	980(10)	965(10)	974(10)
$\tilde{\nu}(AsO_4)$	IR	892 vs 875 vs	918 vs 885 vs	932 m 870 vs	918 vs 874 vs	922 s 868 s	918 vs 872 s
	Raman	923(1) 896(1)	911(8)	910(3) 885(4)	911(5) 881(3)	910(3) 881(2)	911(5)
$\tilde{\nu}(O–O)$	IR	845 vs	849 vs	843 vs	847 vs	843 vs	845 vs
	Raman	857(7)	861(8)	855(8)	858(7)	837(5)	845(4)
$\tilde{\nu}_{asym}[W(O)_2]$	IR	590 s 574 s	594 m 577 s	585 m 569 m	587 m 576 s	584 s 571 s	587 s 573 m
	Raman	593(3) 578(5)	594(2) 579(5)	586(4) 577(6)	589(2) 577(4)	584(4) 573(7)	584(1) 573(3)
$\tilde{\nu}_{sym}[W(O)_2]$	IR	521 s	518 s	511 m	514 s	513 m	517 s
	Raman	535(2)	532(2)	528(2)	530(2)	520(2)	524(1)

[a] Relative intensities in parentheses for Raman data; bands resulting from the quaternary cations and water (complex **5**) are not listed.

the “peroxide class” of ionic compounds with isolated $[O_2]^{2-}$ ions, presents a Raman band at 842 cm^{-1} that is unambiguously assigned to $\tilde{\nu}$(O–O).[52] Hence, spectroscopic data cannot differentiate all the ionic peroxide from the iono-covalent transition-metal complexes. In contrast, the peroxide function has a marked influence on the asymmetric and a less-marked influence on the symmetric stretches of the $\{W(O_2)_2\}$ moieties; their attributions, according to literature data,[50] are given in Table 2 for **4**, **5** and **6**. Two maxima are observed for $\tilde{\nu}_{asym}[W(O)_2]$ that correspond to the structural data (vide supra).

Stoichiometric Epoxidation of (*R*)-(+)-Limonene

The reaction is highly chemoselective and regioselective, i.e. no bis-epoxides, no diols and no 8,9-epoxides were obtained (Scheme 2). Limonene oxide (0.7:1 to 1:1 mixtures of *cis* and *trans* 1,2-epoxide) was characterised and isolated.[13,30] Figure 3 shows that half of the peroxide oxygen is transferred to the olefinic substrate at room temperature, a result which differs from that of the MTO/H_2O_2 systems.[29,53] Comparative experiments with “CH_3ReO_3 + $2H_2O_2$/solvent” show complete transfer of the peroxide oxygen.



Scheme 2. Oxidation products of (*R*)-(+)-limonene.

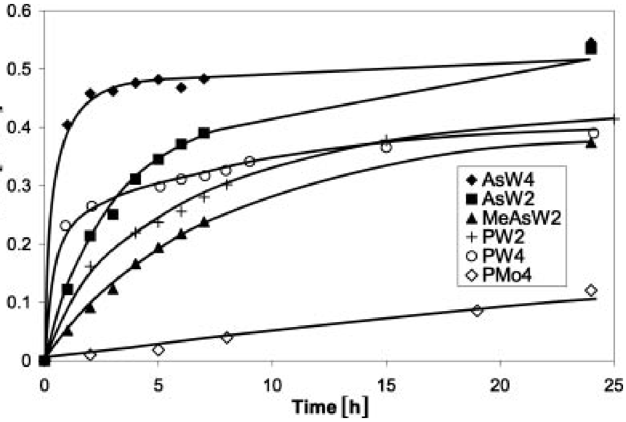


Figure 3. Stoichiometric epoxidation of (*R*)-(+)-limonene. $[(nBu)_4N]^+$ salts, 0.25 mmol for XW_2 and 0.125 mmol for XW_4 or XMo_4; active oxygen content due to oxoperoxo complex = 1 mmol; (*R*)-(+)-limonene: 1.5 mmol; 20 °C; solvent: dry CH_2Cl_2 (5 mL); N_2 ($P \approx 0.1$ MPa), internal standard: *n*-decane.

The kinetic curves also show that $[AsW_4O_{24}]^{3-}$ is more efficient than $[HAsW_2O_{14}]^{2-}$ and that there is a dramatic change from $[PMo_4O_{24}]^{3-}$ to $[AsW_4O_{24}]^{3-}$, which can be correlated with $\tilde{\nu}$(O–O).[13] It appears that the assembling ligand and the metal have a marked influence on the activity of these species, which all initially contain bridging μ-η^2:η^1 peroxo ligands.

It was demonstrated by variable-temperature ^{31}P NMR spectroscopy that $[PM_4O_{24}]^{3-}$ species (M = Mo, W) and even the $[HPW_2O_{14}]^{2-}$ complex are fluxional.[25,43] In these anionic complexes, tridentate peroxo can also bind in a bidentate mode. The rearrangement involves the well-known seven-coordinate and six-coordinate tungsten moieties that were recently characterised;[40] at room temperature, the phosphate anion conserves its tetradentate character of a μ_4-assembling ligand. We cannot run these same NMR spectroscopic experiments with the arsenato analogues, but the structural and spectrometric data related to **2**[10] and **6**, and also to **3**,[13] **4** and **5**,[14] lead us to consider that the phosphatooxoperoxotungstate species and the arsenato analogues behave similarly. Thus, rigid models are only a first approach for the transfer of active oxygen (from peroxo species) to olefinic substrates.[25,43] Rapid equilibria exist between anionic structures with tridentate (μ-η^2:η^1-O_2^{2-}) and bidentate (η^2-O_2^{2-}) modes of coordination for the two kinds of peroxo groups of the $\{M_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ moieties, which play a key role in the activation and transfer of the oxygen of the peroxo groups, probably in the form of $\{\equiv As\text{–}OMO(O_2)_2\}$ and even free $\{MO(O_2)_2\}$ moieties.

Catalysis Tests

Alkene epoxidation catalysed by “AsW_4” peroxo complexes has been investigated by several groups.[11,30,42,43,54] The Arquad 2HT® salts of complexes “AsW_4” and “AsW_2” are active precursors and catalysts in olefin oxidation, and form epoxides in the range 20–60 °C in two-phase “H_2O_2/H_2O/$CHCl_3$ or toluene” systems under phase-transfer catalysis (PTC) conditions (see Table 3, Entries 2 to 4). They transfer active oxygen to (*R*)-(+)-limonene to mostly give the monoepoxides, which are known to be acid-sensitive.[55–57] Complete optimisation must consider the effects of the organic solvent, the nature of Q^+, the assembling ligand X and the anionic species (Cl^-, Br^-, HSO_4^-, etc.), the pH of the aqueous phase, the presence of Na^+Cl^- and the W/X/Q^+ ratios, and these factors have been analysed in detail by several groups.[30,58,59] For example, it has recently been shown that under PTC, a system such as W/$[PO_4]^{3-}$/Q^+ = 2:1:0.4 was more effective than the system 2:1:2 or 4:1:3 corresponding to the onium salts of “PW_2” and “PW_4”, respectively.[31] The use of a large excess of Q^+ leads to low yields and turnover numbers, as shown previously.[30] If a tetra-*n*-hexylammonium cation is used instead of Arquad 2HT®, the conversion is very low (see Table 3, Entry 1).

Comparative studies for the recycling of different catalytic systems for epoxidation are under investigation by our group, and limitations exist for all of them except for the non-chlorinated solvents. Inexpensive buffer systems are

Table 3. (*R*)-(+)-Limonene epoxidation by arsenatooxoperoxotungsten complexes under phase transfer catalysis (PTC) conditions[a] at room temperature after 6 h reaction time.

Entry	$W/[AsO_4]^{3-}/Q^+$	Q^+Cl^-	Organic solvent	Conversion[b] [%]	Selectivity[c] [%]	*Cis* isomer/ *Trans* isomer[d]
1	4:1:3[e]	$(n\text{Hex})_4N^+Cl^-$	Toluene	<1	–	–
2	4:1:2.8	Arquad 2HT®	Toluene	96	50	7.0
3	4:1:2.8	Arquad 2HT®	$CHCl_3$	99	78	1.9
4	2:1:1.4	Arquad 2HT®	$CHCl_3$	98	88	1.2

[a] General PTC procedure: organic solvent (5 mL, 15%); H_2O_2 (4 mL, 19.6 mmol); Teflon-coated bar driven externally by a magnetic stirrer (1200 rpm); limonene (6.2 mmol). [W]/[limonene] = 2%. [b] Conversion based on (*R*)-(+)-limonene was determined by GC using *n*-decane as an internal standard. [c] The selectivity is defined as S = [mol. *cis*- and *trans*-limonene oxide]/[mol. of converted limonene]. [d] See Scheme 2. [e] Catalysis test with **6**.

now easily used and recycled, as well as solid catalysts that are highly resistant to leaching. Note that the use of toluene as the organic solvent instead of $CHCl_3$ leads to a similar conversion but to a lower selectivity towards mono-epoxides (*cis* and *trans*).

Controlled addition of more appropriate weak bases ($Na_2[HAsO_4]$ is used here) to generate a buffer mixture [pK_a ($H_2AsO_4^-/HAsO_4^{2-}$) = 6.95] leads to very high selectivity (>97%), but with a higher reaction time (e.g. 12 h for 99% conversion of limonene at room temperature).

It is clear that certain Keggin-type polyoxometalates can be stable under certain reaction conditions.[26–28] Parameters to consider in this context are solvent, concentrations, pH (more generally the acidity function), temperature, counterions, etc. In this paper, all the species of the catalyst pool, using the dodecatungstate anion as the catalyst precursor, have not been identified. To the best of our knowledge, it is not possible to find spectrometric evidence for all the oxoperoxo complexes. Unfortunately, we cannot perform kinetics or time-resolved studies, and the true catalytic species may be present only at low concentrations and are not amenable to characterisation. It was against this backdrop that we published refs.[25,43]. The catalyst of Noyori et al.[58] is not isolable.

Conclusion

The addition of arsenate to oxoperoxotungstate species (peroxide/tungsten > 2), as well as the use of polyoxometalates such as the Keggin dodecatungstoarsenate anion of $Na_2H[AsW_{12}O_{40}]\cdot nH_2O$ or "AsW_{12}", give, with excess aqueous hydrogen peroxide, arsenatooxoperoxotungstate complexes: $Q_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ or "AsW_4", $Q_2[HAsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ or "AsW_2", etc. isolated with Q^+ = onium cation and $Q'_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$. All these anionic species are highly effective for epoxidation procedures (complete optimisation must consider the effects of the nature of Q^+ or Q'^+, the organic solvent, the assembling ligand X, the pH of the aqueous phase and the $W/X/Q^+$ ratios, as we showed previously).[6,9,30,31] Thus, the heteropolyanion can only be a precursor of the true catalysts (e.g. "AsW_4", "AsW_2", etc.). The "AsW_n" complexes, which have no coordinated water, are lipophilic and are easily transferred into an organic phase with selected Q^+. The facile transfer of active oxygen from these peroxo species to olefinic substrates can be related to their structure and their fluxionality. We propose that the lack of solvolytic stability of "AsW_{12}" and of its analogues in aqueous hydrogen peroxide can be attributed to the equilibria between Keggin and lacunary heteropolyanions and $\{WO_2(OH)\}^+$; this mononuclear group subsequently reacts with H_2O_2 to generate the well-known Mimoun species, $[WO(O_2)_2(H_2O)_2]$, and with X, thus forming "AsW_4", "AsW_2", etc. On the contrary, as shown recently,[7] $[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$ is a preferred catalyst in water for the epoxidation of various allylic alcohols. The crystal structures of "AsW_4", "AsW_2" and of their methylarsenato analogue show that they contain the unique $\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}$ moieties of the Venturello complex.

Experimental Section

Syntheses

$Na_2H[AsW_{12}O_{40}]\cdot NaCl\cdot 30H_2O$: This sodium salt was prepared according to the previously described procedure in which concentrated aqueous HCl (12 M) is used.[51] Note that we found chlorine in the final product, which corresponds to a monohydrogenodisodium salt (yield 72%). $H_{61}AsClNa_3O_{70}W_{12}$ (3566.98): calcd. As 2.10, Cl 0.99, Na 1.93, W 61.85; found As 1.99, Cl 0.84, Na 2.09, W 62.58.

$[(n\text{Hex})_4N]_3[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (6) and $K_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$: This complex was first prepared from the "$H_2WO_4/H_2O_2/H_2O/Na_2H[AsO_4]\cdot 7H_2O/[(n\text{Hex})_4N]Cl$" systems. The synthesis was adapted from methods previously described for the preparation of **6**[60] and **1**, **2**.[9,11] Tungstic acid, "H_2WO_4", (2.5 g, 10 mmol) was added to a 30% aqueous solution of hydrogen peroxide (7 mL, 69 mmol). After 40 min of stirring at 60 °C, and then cooling to room temperature and centrifugation (15 min at 2000 rpm), the supernatant liquid (solution A) was added to an aqueous solution of $Na_2H[AsO_4]\cdot 7H_2O$ (2 mL, 0.78 g, 2.5 mmol). After 15 min of stirring, a solution of $[(n\text{Hex})_4N]Cl$ (1.56 g, 4 mmol) in toluene (25 mL) was slowly added. After 60 min of vigorous stirring, the white precipitate formed at the interface was filtered off, washed thoroughly with distilled water (10 mL), toluene (10 mL) and diethyl ether (10 mL) and dried with P_4O_{10} (yield: 2.82 g, 50%). $C_{72}H_{156}AsN_3O_{24}W_4$ (2258.37): calcd. C 38.29, H 6.96, As 3.32, N 1.86, W 32.56; found C 38.07, H 7.10, As 3.15, N 1.75, W 32.16. IR and Raman spectroscopy: see Table 2. Although tetra-*n*-butylammonium and bis(triphenylphosphoranylidene) ammonium salts were prepared in powder or microcrystalline forms, only the tetra-*n*-hexylammonium salts gave single crystals of an appropriate size from acetonitrile solutions in the presence of a slight excess of hydrogen peroxide, otherwise Keggin salts are formed. Compound **6** was also synthesised from "$Na_2H[AsW_{12}O_{40}]$·$NaCl$·$30H_2O/H_2O_2/H_2O/[(nHex)_4]Cl$ or $[(nBu)_4N]Cl$" systems. Aqueous hydrogen peroxide (30%, 100 mmol; 10 mL) was slowly added to a solution of the $[AsW_{12}O_{40}]^{3-}$ salt (vide supra, 0.5 mmol, 1.57 g) in water (1 mL). After 30 min of stirring at room temperature, an aqueous solution of tetra-*n*-butylammonium chloride (3 mL, 1.6 mmol, 0.45 g) was slowly added. The white precipitate was filtered off, washed with water (2 × 10 mL) and then dried with P_4O_{10} (yield: 0.47 g, 41.5% based on As). Higher yields (≥90%) were obtained when an excess of $Na_2H[AsO_4]$·$7H_2O$ was added to the aqueous phase. Excess potassium chloride (7 mmol) can also be added to the recovered filtrate. A few millilitres of ethanol were added to the solution that was cooled to 5 °C until a snow-white precipitate appeared. After filtration and washing with ethanol, the precipitate, $K_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]$·$2H_2O$, was air dried (yield 60% based on the initial precursor). See Scheme 1 for the appropriate choice of counteranions in order to obtain the two oxoperoxo salts selectively.

$[(nBu)_4N]_2[HAsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (4): Solution A (vide supra) and a solution of $Na_2H[AsO_4]$·$7H_2O$ (1.59 g; 5.1 mmol) in water (2 mL) were mixed at room temperature. After 20 min of stirring, an aqueous solution of $[(nBu)_4N]Cl$ (2.78 g, 10 mmol in 10 mL) was slowly added while slow stirring was maintained. The white precipitate was filtered off on a fritted glass disc, washed thoroughly with cold water (10 mL) and diethyl ether (10 mL) and dried with P_4O_{10} (yield: 4.46 g, 77%). $C_{32}H_{73}AsN_2O_{14}W_2$ (1152.56): calcd. C 33.34, H 6.38, As 6.50, N 2.43, W 31.90; found C 33.49, H 6.45, As 6.15, N 2.55, W 30.92. IR and Raman spectroscopy: see Table 2. (Compound **4** can also be prepared from $[AsW_{12}O_{40}]^{3-}$, but it is more convenient to use a direct method).

$[(nBu)_4N]_2[CH_3AsO_3\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]$ (5): This was prepared in a similar manner. $Na_2[CH_3AsO_3]$·$6H_2O$ (1.49 g, 5.1 mmol), dissolved in water (2 mL), was added to solution A. After 30 min of stirring $[(nBu)_4N]Cl$ (2.78 g in 7.5 mL water) was slowly added. Well-formed crystals suitable for X-ray measurements were obtained by slow evaporation of acetonitrile/H_2O_2 solutions of the microcrystalline precipitates of **4** and **5**.[14]

Structure Determinations: Single crystals of **6** were grown from $CH_2Cl_2/(C_2H_5)_2O/H_2O_2$ (2:1:0.1), or better from $CH_3CN/H_2O_2/H_2O$ mixtures, by slow evaporation at +5 °C. Although highly precise crystal structure analyses are not easily obtained with the tetra-*n*-hexylammonium cation[9,10] (a result of the flexibility of the long alkyl chain, solvent molecules that are incorporated in the crystals and disorder for some of the cations[61]), X-ray measurements were undertaken, because, at least, the structure of the anion could be elucidated, which would provide valuable information for the chemistry of heteropolyanions containing the $[AsO_4]^{3-}$ assembling ligand and for the relationship of some Keggin anions and Venturello–Ishii systems.

$[(nHex)_4N][AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]$ (6): $C_{72}H_{156}AsN_3O_{24}W_4$, $M_r = 2258.37$, monoclinic, space group *C*2 (no. 5); $a = 2051.6(6)$, $b = 1592.3(4)$, $c = 1490.2(2)$ pm, $\beta = 91.64(1)°$, $V = 4.866(1)$ nm^3, $Z = 2$, $\rho_{calcd.} = 1.54$ Mg m^{-3}, $F(000) = 2260$, $\lambda = 71.073$ pm, $T = 293$ K, $\mu(Mo\text{-}K_\alpha) = 0.5112$ mm^{-1}, crystal dimensions 0.1 × 0.3 × 0.4 mm (parallelepiped), $2° \leq 2\theta \leq 50°$, 13697 measured reflections, 7412 were unique, 206 parameters refined in full-matrix, $R_1 = 0.058$ with 5318 reflections $[I > 3\sigma(I)]$, $wR_2 = 0.067$, $w \neq 1$ [weighting scheme of the form $w = w'[1 - \{(||F_o| - |F_c||)/6\sigma(F_o)\}^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 0.417, 0.302 and 0.177 for a Chebyshev series for which $X = F_c/F_{c(max)}$].[62] Min./max. residual electron density –127/153 e mm^{-3}. Goodness of fit: 0.93. The data were collected with a KAPPACCD-Enraf Nonius automated diffractometer at room temperature. (At low temperature the crystal collapsed.) Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 35 well-centered reflections. Corrections were made for Lorentzian and polarization effects; an absorption correction (sadabs) was also applied. The structure was solved by direct methods (SHELX-86 program)[63] and subsequent Fourier difference techniques. Some of the carbon atoms of the ammonium counterions showed high thermal parameters as a result of the flexibility of the long alkyl chain and were not refined, even with reduced occupancy. Only 34 carbon atoms could be well located in the difference Fourier map. These problems probably arise from low-solvent content and from the fact that the crystal decomposes slowly. Computations were performed using CRYSTALS,[64] adapted to a PC computer. Atomic form factors for neutral C, N, As, O and W were taken from ref.[65] Refinements were carried out by minimising the functions $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $Rw^* = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w F_o{}^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively. A representation of the anion was drawn with CAMERON[66] (see Figure 1).

CCDC-276917 for **6** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General: The solvents were purified by standard procedures for the stoichiometric and catalytic tests. Commercial, stabilised 30% w/v aqueous solutions of hydrogen peroxide (pH ≈ 1.5) either contained a phosphorus(V) concentration lower than 1.5 mM or were without phosphates (Aldrich) in order to avoid the formation of phosphatooxoperoxotungstate species. Tungstic acid, "H_2WO_4" was supplied by Eurotungstène. $Na_2H[AsO_4]$·$7H_2O$ and $Na_2[CH_3AsO_3]$·$6H_2O$ were obtained from Prolabo/VWR. The onium salts are marketed by Aldrich and Lancaster Synthesis. (*R*)-(+)-Limonene (Lancaster) was shown to be more than 97% pure by GC and NMR analyses. GC analyses were carried out with a Girdel chromatograph (FID) fitted with a SPB™ 1701 capillary column with helium as the carrier gas. Analyses were performed at temperatures ranging from 70 to 200 °C (5 °C min^{-1}, P_{He}: 0.16 MPa). GC–MS analyses were performed with a GC apparatus coupled with a mass spectrometer (Girdel 30/Delsi-Nermag and Trace GC 2000 series-Thermofinnigan) coupled to a Trace MS mass spectrometer (EI or CI/NH_3). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature with a Fourier transform apparatus (Bruker AC 200), using $CDCl_3$ as the solvent and TMS as the internal reference. IR spectra (resolution: 2–4 cm^{-1}) were measured with a Fourier transform apparatus (Bruker IFS 45 or Equinox 55) in Nujol suspension, either between two caesium bromide plates or KBr pellets. Solution spectra of **4**, **5** and **6** in acetonitrile (0.05 M) were recorded at room temperature with a standard sodium chloride cell (0.1 mm thickness). Acetonitrile has a window between 500–910 cm^{-1}, which is suitable for studying $\tilde{\nu}$(O–O), $\tilde{\nu}_{sym}[W(O_2)]$ and $\tilde{\nu}_{asym}[W(O_2)]$ bands.

Raman spectra were recorded at room temperature with a Jobin–Yvon U1000 spectrometer with a resolution of 4 cm^{-1}. Solid samples of the complexes were mounted on a disc rotating at about 1000 rpm in order to avoid decomposition and/or photoreduction by the laser beam (excitation line, 514.5 nm of an Ar$^+$ laser; source power, 30–50 mW; scanning time, ca. 2 h). Solutions of **6** (0.25 M), **4** (0.5 M) and **5** (0.5 M) were studied. Elemental analyses (C, H, As, N and W) were carried out at the Service Central d'Analyses CNRS, Vernaison.

Stoichiometric Regioselective Epoxidation with Six Oxoperoxo Complexes: These were conducted under dinitrogen using Schlenk techniques and deaerated solvents. (*R*)-(+)-Limonene (1.5 mmol) was rapidly added to a thermostatted (20 °C) solution of the complex (0.25 mmol for XW_2 and 0.125 mmol for XW_4 or XMo_4, active oxygen content, i.e. $[O_2]^{2-}$: 1 mmol) in dry CH_2Cl_2 (5 mL). The solution was stirred under dinitrogen. GC analyses were performed periodically with *n*-decane as internal standard. (*R*)-(+)-Limonene oxide (mixture of *cis* and *trans*) was obtained and isolated. It was identified by MS and by ^{1}H and ^{13}C NMR spectroscopy.[13]

Catalysis Tests: Our previous procedure[13,23] was followed. "H_2WO_4" was treated with 15% H_2O_2 (4 mL, 19.6 mmol). After 15 min of stirring (necessary for the precursor to react completely at 60 °C) and cooling at room temperature, $Na_2H[AsO_4]\cdot 7H_2O$ was added (see Table 3). Q^+Cl^-, dissolved in the organic solvent, was then added with the substrate (6.2 mmol). The two-phase mixture was stirred vigorously (1200 rpm) for 6 h at 20 °C under dinitrogen. The organic extract was analysed by GC and/or GC–MS and in some cases by ^{1}H NMR spectroscopy.

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