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Reinvestigation of Epoxidation Using Tungsten-Based Precursors and Hydrogen Peroxide in a Biphase Medium

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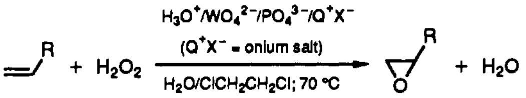
The reaction of hydrogen peroxide with tungstic acid, "H_2WO_4", and various types of polyoxometalates (isopolyanions, $[M_nO_y]^{x-}$, and heteropolyanions, $[XM_{12}O_{40}]^{x'-}$ and $[X_2M_{18}O_{62}]^{x''-}$, where M = Mo and W and X = P, B, and Si) has been studied by several physicochemical techniques (UV, IR, Raman, and ^{31}P and ^{183}W NMR spectroscopy). On the basis of these results, an interpretation of the differences in the catalytic activity of these precursors in the epoxidation of 1-octene by H_2O_2 in a biphase medium is proposed. Heteropolyacids (HPA) with the Keggin structure, $H_3[PM_{12}O_{40}]$ (M = Mo, W), are degraded in the presence of excess H_2O_2 to form peroxo species $\{PO_4[M(O)(O_2)_2]_4\}^{3-}$ and $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$. These anions were isolated in the form of salts and identified by elemental and spectroscopic analyses; it appears that the former is responsible for the catalytic activity of phase-transfer systems involving $H_3[PM_{12}O_{40}]$ as a precursor.

Polyoxometalates, in particular those with the Keggin structure, have been used in recent years for the selective oxidation of organic substrates with dioxygen,[1–4] alkyl hydroperoxides,[5,6] PhIO,[7] and hydrogen peroxide.[8–10] It has long been known that, with hydrogen peroxide, more simple materials containing molybdenum or tungsten are also effective in homogeneous catalytic systems.[11,12]

More recently, an original catalytic epoxidation process with solutions of hydrogen peroxide under phase-transfer conditions (PTC) was reported by Venturello et al.:[13]



Related systems, for example those involving tungstic acid, "H_2WO_4", as a precursor, also lead to high activities.[14] Under phase-transfer-reaction conditions, which are particularly suited to nonfunctionalized terminal olefins, such anionic species as $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ [13b] or $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ [14b] have been proposed as active oxygen-to-olefin transfer agents in association with an onium salt; the former is also a stoichiometric oxidizing agent.[13b]

In a very similar approach, polyoxometalates based on molybdenum or tungsten have been used recently in systems operating under phase-transfer conditions. Thus, Ishii et al.[9c] studied the epoxidation of olefins with heteropolyacids, HPA, $H_n[XM_{12}O_{40}]$ (X = P, Si; M = Mo, W), with the Keggin structure, in the presence of a quaternary ammonium chloride. The formation of polynuclear peroxo species from $H_3[PM_{12}O_{40}]$ was proposed, but these cannot yet be completely identified.[9,15–17] At first sight, the lack of reactivity of $H_4[SiW_{12}O_{40}]$[9c] is difficult to understand.

From these results, it is not clear whether the peroxo complexes formed from HPAs are really more active than those obtained from tungstic acid, "H_2WO_4", or those obtained by association of PO_4^{3-} and WO_4^{2-}. First, in order to compare the catalytic activities of some polyoxometalates and other precursors, we employed 1-octene as the model substrate and used the epoxidation reaction with hydrogen peroxide under phase-transfer-catalysis conditions.

On the basis of initial results, we could not establish a clear relationship between the structure of the starting polyoxometalate and catalytic activity. In an attempt to interpret these results, we have analyzed the aqueous and organic phases by various physicochemical methods and isolated some salts, in order to confirm the spectroscopic analysis of the solutions (Raman, visible, UV, and ^{31}P and ^{183}W NMR spectroscopy).

Results

Epoxidation tests on 1-octene with hydrogen peroxide in a biphase medium ($H_2O/CHCl_3$) were performed in the presence of polyoxometalates, some of which had already been used in earlier work: $[Mo_7O_{24}]^{6-}$,[8] $[PM_{12}O_{40}]^{3-}$ (M = Mo, W).[9c] In addition, other precursors with oxo groups, such as "H_2WO_4" or a mixture Na_2WO_4/H_3PO_4, were included for a comparative study. In all cases, the phase-transfer agent was a quaternary ammonium chloride, Arquad 2HT (see Experimental Section). The results obtained are reported in Table I.

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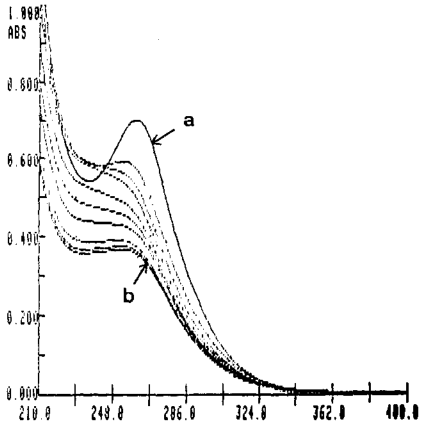

Figure 1. UV absorption spectra in H_2O showing evolution of the $H_3[PW_{12}O_{40}]/H_2O_2$ system ($[H_2O_2]/[W] = 40$): (a) $t = 0$ (no H_2O_2); (b) $t = 60$ min.

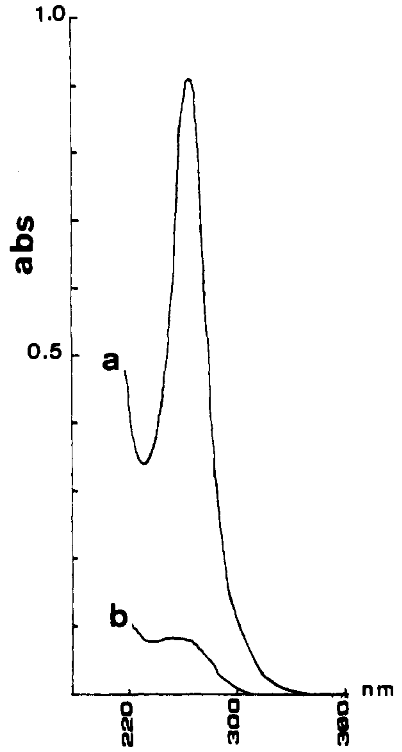

Figure 2. UV absorption spectra in $ClCH_2CH_2Cl$ (organic phases of biphase media) of the $H_3[PW_{12}O_{40}]/Q^+Cl^-/H_2O_2$ system (molar ratios 1/3/800) with procedure A (a) and procedure B (b). (The UV spectrum of the diluted organic phase was recorded after 2 h of reflux).

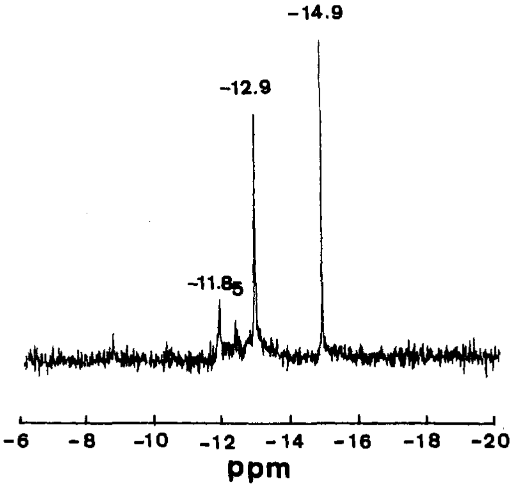

Figure 3. 101.2-MHz ^{31}P NMR spectrum of the species transferred by Arquad 2HT in $CDCl_3$ from $H_3[PW_{12}O_{40}]/H_2O_2$ (molar ratio 1/12) after 45 min evolution in aqueous medium.

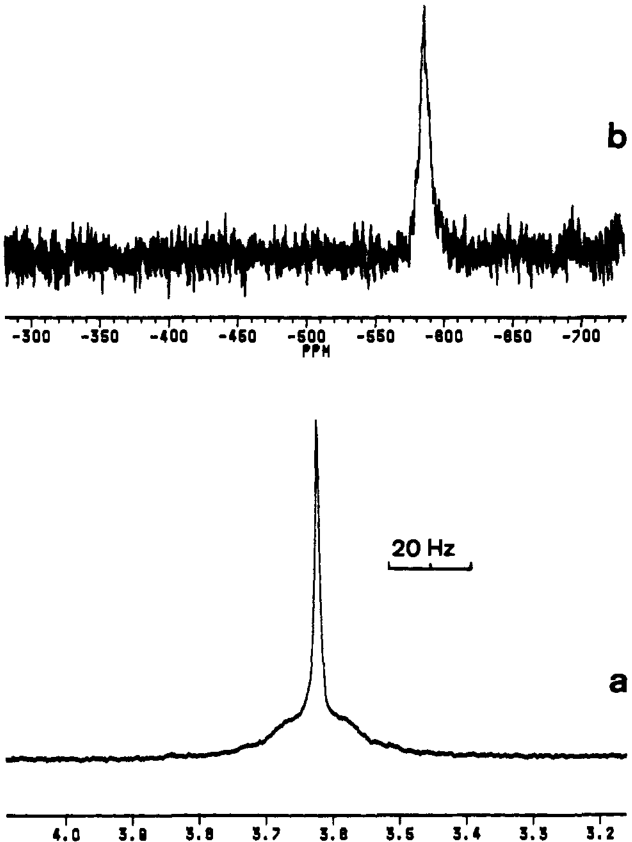

Figure 4. ^{31}P and ^{183}W NMR spectra of a $CDCl_3$ solution of $Q_3\{PO_4[WO(O_2)_2]_4\}$ prepared from $H_3[PW_{12}O_{40}]/H_2O_2$ (molar ratio 1/500): (a) 162-MHz ^{31}P spectrum (380 scans, without exponential multiplication); (b) 16.6-MHz ^{183}W spectrum (8160 scans, line broadening 5 Hz). $Q^+ = \{[(C_{18}H_{37})\ (75\%) + (C_{16}H_{33})\ (25\%)]_2N(CH_3)_2\}^+$.

A UV study was performed, since most of the polyoxometalates have characteristic spectra in the middle of the ultraviolet range. We examined the interaction between hydrogen peroxide and polyoxometalates in an aqueous medium. The data in Table II include the main observations (Figure 1). This study was supplemented by a study of anionic species, transferred to an organic phase with a quaternary ammonium salt. The UV spectrum of the organic phase (Figure 2) was recorded to interpret the quite different behavior of $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ and the effects of two procedures; vide infra.

Some of the peroxo complexes formed with various concentrations of hydrogen peroxide were identified by ^{31}P and ^{183}W NMR spectroscopy. With low concentrations of hydrogen peroxide ($[H_2O_2]/[W] \simeq 1$) typical ^{31}P NMR spectra showed new signals in the −11 to −13 ppm region (Figure 3). Dramatic changes are observed if $[H_2O_2]/[W]$ is increased; the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ anion (Figures 4 and 5) was characterized by NMR spectroscopy for the first time in the biphase system under these conditions.

A complementary Raman spectrometric study was performed to confirm the results obtained by UV and NMR spectroscopy and in order to identify the species formed from the $H_3[PW_{12}O_{40}]/H_2O_2$ mixtures (Figures 6 and 7).

Discussion

Catalytic Tests. The results given in Table I show a wide range of activities depending on the nature of the precursor and on experimental details (see Experimental Section). For the five

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Table I. Epoxidation of 1-Octene with H_2O_2 Catalyzed by Molybdenum- or Tungsten-Based Precursors under Phase-Transfer Conditions[a]

run	precursor[b]	$[Q^+Cl^-]^a/[M]$ (M = Mo, W)	experimental procedure;[c] time, h	epoxide yield,[d] %	H_2O_2 conversion,[e] %
1	$H_5[BW_{12}O_{40}]$	0.42	A; 24	0	0
			B; 24	0	34
2	$H_4[SiW_{12}O_{40}]$	0.33	A; 21	0	
			B; 23	traces	
3	$H_3[PMo_{12}O_{40}]$	0.25	A; 23	1	22
			B; 23	8	64
4	$H_3[PW_{12}O_{40}]$	0.25	A; 5	0	13
			B; 5	79	67
5	$H_6[P_2W_{18}O_{62}]$	0.33	A; 22	0	7
			B; 22	0	0
6	$K_4[W_{10}O_{32}]$	0.26	A; 5	traces	1
			B; 5	9	10
7	$(NH_4)_{10}[H_2W_{12}O_{42}]$	0.26	A; 17	67	95
			B; 5	52	42
8	$(NH_4)_6[Mo_7O_{24}]$	0.88	A; 24	16	68
			B; 24	11	64
9	"H_2WO_4"	0.27	A; 5	75	65
			B; 5	76	73
10	Na_2WO_4/H_3PO_4[f] (1/5)	0.35	A; 5	20	13
			B; 5	25	25

[a] General procedure for epoxidation under PTC: $CHCl_3$ (5 mL)/10% H_2O_2 (3 mL; 9.8 mmol) at 60 °C; Teflon-coated bar driven externally by a magnetic stirrer; 1-octene (6.5 mmol); $[M]/[\text{1-octene}]_0 \simeq 2\%$ (M = Mo, W); phase-transfer agents (Q^+Cl^-) = Arquad 2HT (obtained from Akzo) = $\{[(C_{18}H_{37})_2\ (75\%) + (C_{16}H_{33})_2\ (25\%)]N(CH_3)_2\}^+Cl^-$. $[Q^+]/[M]$: see column 2. $1.0 < pH_0 < 1.6$. [b] Representations of coordination polyhedra are well-known; see for example $\alpha - [X^xM_{12}O_{40}]^{8-x}$,[18] $[X_2M_{18}O_{62}]^{y-}$,[19] $[W_{10}O_{32}]^{4-}$,[20] $[H_2W_{12}O_{42}]^{10-}$,[21] and $[Mo_7O_{24}]^{6-}$.[22] [c] Two experimental procedures: A = "one-spot system"; B = preformed catalytic system (see Experimental Section). [d] Yields based on 1-octene were determined by GC by using an internal standard (anisole); selectivity > 95%. [e] Iodometric titration (KI; $Na_2S_2O_3$). [f] See ref 13c.

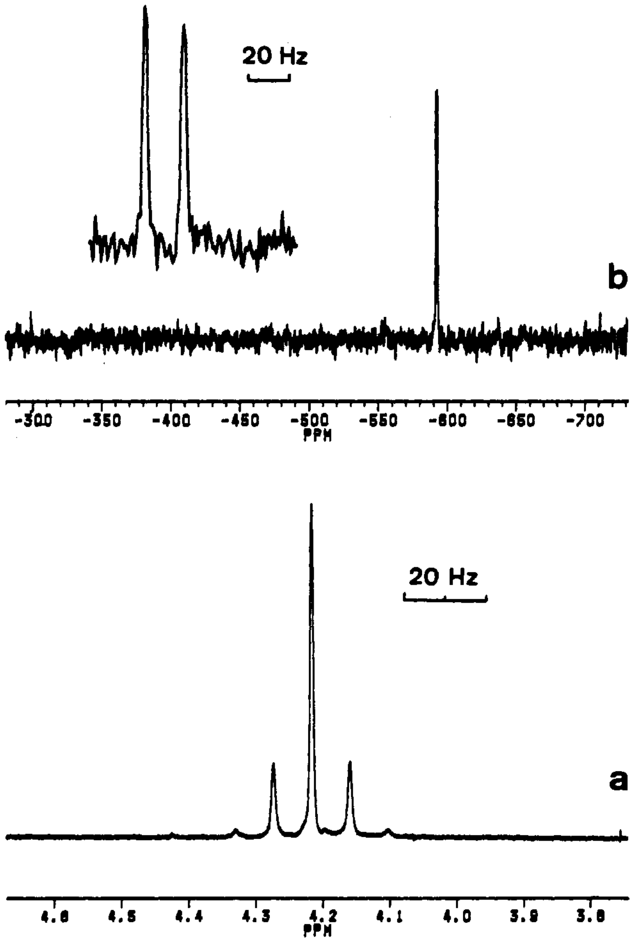

Figure 5. ^{31}P and ^{183}W NMR spectra of a $CH_3CN/CDCl_3$ (90/10) solution of $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ precipited from a $H_3[PW_{12}O_{40}]/H_2O_2$ mixture (molar ratio 1/500): (a) 162-MHz ^{31}P spectrum (48 scans, without exponential multiplication); (b) 16.6-MHz ^{183}W spectrum (737 scans, line broadening 1 Hz).

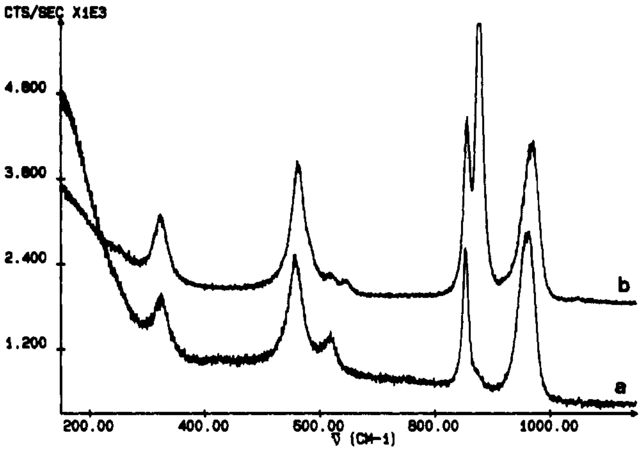

Figure 6. Raman spectra: (a) $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ in H_2O; (b) $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in dilute H_2O_2.

Figure 7. Raman spectra in H_2O of $H_3[PW_{12}O_{40}]$: (a) no H_2O_2; (b) $[H_2O_2]/[W] = 1$; (c) $[H_2O_2]/[W] = 15$.

heteropolyacids (entries 1–5), procedure A, in which hydrogen peroxide is introduced after transfer of the precursor to the organic phase (in the form of a quaternary ammonium salt), does not lead to catalytic systems. The olefin is not epoxidized, while the hydrogen peroxide is not, or is only partially, consumed.

In contrast, if the hydrogen peroxide is mixed with the heteropolyacid in an aqueous solution *before the two phases are mixed*

Table II. Absorption Spectral Data for Polyoxometalate/H_2O_2 Systems[a]

run	precursor	H_2O solution:[c] λ_{max} (ϵ_{max})[b]	H_2O_2 solution:[d] $[H_2O_2]/[M]$	spectral change	λ_{max} (ϵ_{max})[b]
1	$H_5[BW_{12}O_{40}]$	256 (3450)	355	–	
2	$H_4[SiW_{12}O_{40}]$	262 (3550)	355	–	
3	$H_3[PMo_{12}O_{40}]$	<220	30	+	309 (900)
4	$H_3[PW_{12}O_{40}]$	260 (3200)	30	+	252 (1500)
5	$H_6[P_2W_{18}O_{62}]$	300 and 250 (2 sh)	355	–	
6	$K_4[W_{10}O_{32}]$	319 (400), 260 (sh)	350	–	
7	$(NH_4)_{10}[H_2W_{12}O_{42}]$	smooth curve	90	+	251 (1100)
8	$(NH_4)_6[Mo_7O_{24}]$	smooth curve	90	+	312 (900) 227

[a] General procedure: C_{Mo} or C_W = 2–3 mmol L^{-1}; cell path 1 mm. The measurements were made before the addition of H_2O_2 and 2–60 min after the solutions were mixed. [b] λ_{max} in nm; ϵ in L cm^{-1} (mol of Mo or W)$^{-1}$. [c] H_2O in the reference cell. [d] H_2O_2 in the reference cell.

(procedure B), then $H_3[PMo_{12}O_{40}]$ (entry 3) and especially $H_3[PW_{12}O_{40}]$ (entry 4) do have catalytic activity. Of the four Keggin type HPAs, only those with a central PO_4^{3-} anion are active (entries 1–4, with procedure B only). However, the effects of structure and/or the charge density of the entire anion must also be considered, since the Dawson type HPA, $H_6[P_2W_{18}O_{62}]$, is inactive under the same conditions (entry 5).

For two of the isopolyanions (entries 7 and 8 but not entry 6), the catalytic activity appears to be slightly less dependent on the experimental procedure. The yield of epoxide after 5 h of reaction with $K_4[W_{10}O_{32}]$ is significantly improved by using procedure B but still remains low (entry 6) compared to that obtained with $(NH_4)_{10}[H_2W_{12}O_{42}]$ (entry 7).

The results of the catalytic tests suggest that the difference in activity between the ammonium "paratungstate B", $(NH_4)_{10}[H_2W_{12}O_{42}]$, and tungstic acid, "$H_2WO_4$", could arise from the fact that the active species differ in their nature or their relative concentrations in the aqueous and organic phases. As there is almost no variation in the initial pH (1.0–1.6) from one experiment to another, it is also possible to imagine that there is a salt effect related to K^+ or NH_4^+. The three corresponding isopolyacids (entries 6–8) have not been isolated; however, we note, as do other authors,[9c] that acid precursors prove to be more efficient for this type of catalysis. Furthermore, the various isopolyoxometalates are stable only under certain conditions of pH, ionic strength,[23] solvent,[24] initial metal concentration,[25a] temperature,[25a] associated cation,[25] concentration of the nucleophilic species, etc., and so it is not certain that the precursors involved are stable in the reaction medium.

Finally, it is important to note that phosphotungstic acid, $H_3[PW_{12}O_{40}]$ (entry 4), is the most active of the eight polyoxometalates (entries 1–8) but that, under the experimental conditions used, its catalytic activity is close to that obtained with tungstic acid (entry 9). The performances of the combined sodium tungstate and orthophosphoric acid precursor proposed by Venturello et al.[13c] are, under these conditions (entry 10), much poorer than those obtained with tungstic acid or even with phosphotungstic acid. With the preformed catalyst $(Q)_3\{PO_4[WO(O_2)_2]_4\}$ results are improved (epoxide yield = 54% if $Q^+ = Hex_4N^+$ and 60% with Arquad 2HT after 6 h).

Ultraviolet Absorption Spectrometry. The absorption bands of the UV spectra of most polyoxometalates (hetero- and isopolyanions based on tungsten or molybdenum) have been attributed to charge-transfer oxygen to the metal M (W(VI) or Mo(VI)). In particular, between 250 and 350 nm absorption is thought to be due to M–O–M chromophores;[26] consequently, we selected this wavelength range. In fact, the spectra in this region are very characteristic of the polyanionic structure; thus, the Keggin type HPAs based on tungsten have an absorption peak near 260 nm ($\epsilon \approx 3000$ L cm^{-1} (mol of W)$^{-1}$) (Figure 1).

Each polyoxometalate was dissolved in water at a suitable concentration (see Table II) and then treated with an excess of hydrogen peroxide ($30 \leq [H_2O_2]/[M] \leq 355$). The UV spectra of the aqueous solution and of those obtained with hydrogen peroxide are compared (Table II).

In some cases, after the addition of excess hydrogen peroxide, there is almost no variation in the UV spectrum (Table II, entries 1, 2, 5), while, in others, there is a pronounced more or less rapid change (Figure 1 and Table II, entries 3, 4, 7, and 8).

To study the species resulting from the action of hydrogen peroxide, it would be of interest to have the spectra of the known peroxo species likely to be formed in this medium. We therefore obtained the spectra of $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ (M = Mo, W) and of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (the related combination with molybdenum is not described). The two peroxotungstates, prepared according to described procedures,[13b,27b] cannot be unambiguously differentiated by their electronic transition spectra. In fact, for $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$,[27b] we find an absorption band at 240 nm (ϵ = 1100 L cm^{-1} (mol of W)$^{-1}$), in agreement with literature data,[28] whereas, for tetrakis(oxodiperoxotungsto)phosphate(3–), the absorption peak is at 252 nm (ϵ = 1250 L cm^{-1} (mol of W)$^{-1}$). For the anion $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$, there are two bands,[28] one at 311 nm ($\epsilon \approx 1000$ L cm^{-1} (mol of Mo)$^{-1}$) and the other at 237 nm ($\epsilon \approx 2000$ L cm^{-1} (mol of Mo)$^{-1}$). It is precisely these two peaks that are seen when ammonium heptamolybdate is treated with an excess of hydrogen peroxide.[29] It appears therefore that this isopolyanion is rapidly degraded under the conditions employed for epoxidation (entry 8).[16]

In the case of isopolytungstate $(NH_4)_{10}[H_2W_{12}O_{42}]$, degradation by hydrogen peroxide also very probably leads to $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (entry 7). In the same way, attack on $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ by hydrogen peroxide was detected (entries 3 and 4), but no peroxo species has yet been identified. Peroxotungstates and/or phosphoperoxotungstates may well be involved. *It is to be stressed that the four precursors which lost their polyanionic structure in the presence of excess hydrogen peroxide* (Table II, entries 3, 4, 7, and 8) *lead to considerable activity* (Table I, entries 3, 4, 7, and 8).

The three heteropolyacids without any catalytic activity (Table I, entries 1, 2 and 5) apparently retain their polyanionic structure, even in the presence of an excess of hydrogen peroxide ($[H_2O_2]/[W] \approx 350$) (Table II, entries 1, 2, and 5). It must be noticed that very drastic conditions ($[H_2O_2]/[W] \simeq 8000$; H_2O_2 70%) are necessary to degrade $H_4[SiW_{12}O_{40}]$.[30] Of these eight polyoxometalates, $K_4[W_{10}O_{32}]$ (entry 6) is the only one for which there is no correlation between catalytic activity and a change in the UV spectrum. However, with this precursor the catalytic epoxidation reaction is very slow and this may also be the case for the degradation of the polyanion. Given the complexity of

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the equilibria between isopolytungstates,[31] we did not attempt to study these systems further (entries 6–8).

To examine the species transferred into the organic phase with a quaternary ammonium salt in a biphase system, we used $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$; the first doubtless undergoes some transformation in the presence of hydrogen peroxide, whereas the second is apparently stable (see above: $[H_2O_2]/[W] \simeq 350$). Systems comparable to those of the catalytic tests (Table I) were studied without any substrate and with a biphase $H_2O/ClCH_2CH_2Cl$ medium (the latter is UV transparent at shorter wavelengths than $CHCl_3$). The UV spectrum of the suitably diluted organic phase was recorded after 2 h of reflux (Figure 2).

For $H_4[SiW_{12}O_{40}]$, whatever the experimental procedure employed, the resulting UV spectrum is characteristic of the polyanionic structure ($[H_2O_2]/[W] \simeq 80$). In addition, it appears that almost all the tungsten is in the organic phase; $Q_4[SiW_{12}O_{40}]$ is stable and inactive in this phase (Table I, entry 2). This is also the case for $H_3[PW_{12}O_{40}]$ with experimental procedure A where the polyanion is transferred into the organic phase before the addition of hydrogen peroxide.[32] Nevertheless, in contrast to $H_4[SiW_{12}O_{40}]$, it is possible to activate $H_3[PW_{12}O_{40}]$ by procedure B, in which HPA is treated in the aqueous phase with an excess of hydrogen peroxide (Table I, entry 4). In this case, we have just seen that the activation process is accompanied by HPA degradation. A species or the species resulting from the rapid interaction of $[PW_{12}O_{40}]^{3-}$ with excess H_2O_2 is/are transferred in part into the organic phase. Indeed, the absorption peak is at about 250 nm and the molar absorption coefficient can be estimated at 1000 L cm^{-1} (mol of $W)^{-1}$ (if we assume formation of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and/or $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, the amount of quaternary ammonium salt used only allows about one-fourth to one-third of the tungsten to be transferred).

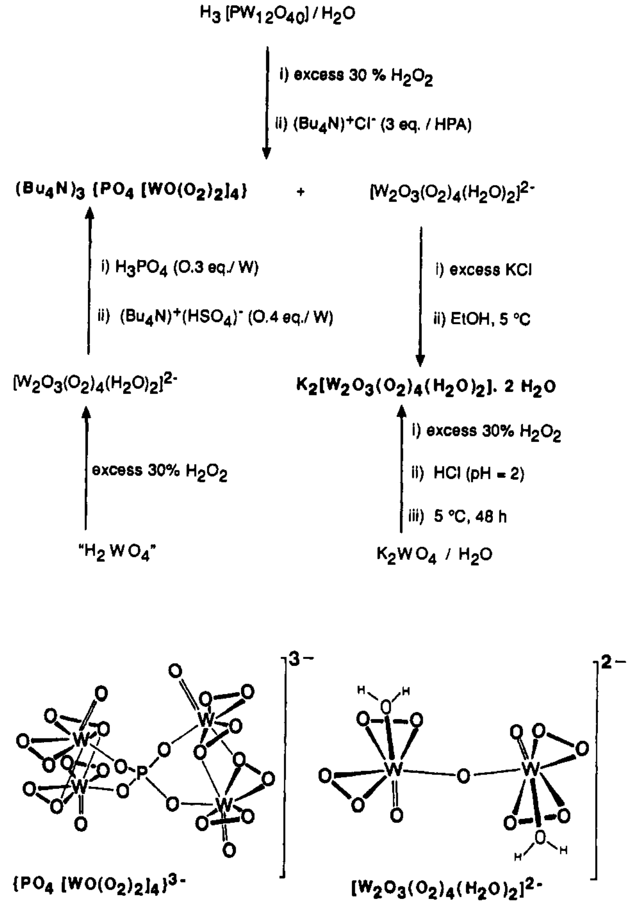
On the basis of these experiments, we were able to interpret the results of the catalytic tests as follows: the HPAs considered here can be used as oxidation precursors with hydrogen peroxide in a biphase medium *only if a prior interaction of HPA with excess hydrogen peroxide leads to the formation of less condensed peroxo structures*, whose identification requires other techniques.

^{31}P and ^{183}W NMR Spectra. The long-term stability of the yellow color of aqueous solutions ($[H_2O_2]/[PW_{12}O_{40}]^{3-} \leq 24$) led us to investigate these systems with *low H_2O_2 concentration* by ^{31}P NMR spectroscopy. Under the conditions $[H_2O_2]/[W] \simeq 1$, and after 45-min reaction at room temperature, the anionic species were transferred into the organic phase with Arquad 2HT (the yellow solute passes from the aqueous phase to the organic phase). The ^{31}P NMR spectrum shows several peaks (Figure 3). The strongest line at −14.9 ppm is attributed to $[PW_{12}O_{40}]^{3-}$;[33a] another strong resonance is observed at −12.9 ppm with small signals at δ −12.4 and -11.8_5 ppm. These latter signals can be attributed to HPA with peroxo groups, in agreement with the observation of Soviet workers for aqueous solution.[15] These anions are probably intermediates in the degradation process in the presence of excess hydrogen peroxide. In our case, the -11.8_5 ppm line persisted for aqueous solutions after 6 months of standing; the ^{183}W NMR spectrum consisted of several lines, some of which are characteristic of W^{VI} in hexacoordination (−100 to −200 ppm)[33b] and some are related to $W(O_2)$ moieties (ca. −500 ppm).[27b] This system is currently being studied.[30]

To complete the studies of systems in the aqueous phase or in a biphase medium, peroxo complexes resulting from the interaction of $[PM_{12}O_{40}]^{3-}$ (M = Mo, W) and *excess hydrogen peroxide* were isolated in the form of quaternary ammonium or alkali-metal salts.

Peroxo species have already been synthesized[9c] from these HPAs and cetylpyridinium chloride, but they have not been completely characterized. In particular, the analytical data are very different from those expected from a formula derived from the Keggin structure, i.e. $[C_5H_5N(CH_2)_{15}CH_3]_3[PM_{12}(O)_{40-x}(O_2)_x]$ (M, x = Mo, 6 or W, 5). According to the synthetic procedures,[9c] the heteropolyanion (as an acid or salt) is left in contact with excess hydrogen peroxide for a few hours at 40 °C. We have just seen that the species formed in this way contain fewer than 12 Mo or W atoms in the cluster anion.

Scheme I. Synthesis of Anionic Peroxo Complexes



We more thoroughly examined the case of $H_3[PW_{12}O_{40}]$, one of the most active water-soluble precursors in epoxidation catalysis. To precipitate the anions formed from $[PW_{12}O_{40}]^{3-}$ and excess H_2O_2, we added tetrabutylammonium chloride and isolated the complex $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ and potassium chloride, which gave $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$. Therefore, the appropriate choice of counteranions allowed us to obtain the two peroxo salts selectively (Scheme I). The products have been characterized by active oxygen assay, elemental analysis, and ^{31}P and ^{183}W NMR spectroscopy. Their properties match those of authentic salts prepared as described.[13d,27b] In particular, the ^{31}P NMR spectrum of $(Bu_4N)_3\{PO_4[WO(O_2)_2]_4\}$ prepared with $H_3[PW_{12}O_{40}]$ according to Scheme I revealed a single line at +4.2 ppm; no other signals were detected between +10 and −30 ppm. This indicates that the transformation was complete. In the chloroform ($CDCl_3$) solution of the Arquad 2HT species, the ^{31}P line ($\Delta\nu_{1/2}$ = 1.5 Hz) was flanked by broad unresolved humps (Figure 4a) and the ^{183}W spectrum revealed a broad resonance ($\Delta\nu_{1/2}$ = 80 Hz) at −586 ppm (Figure 4b). For the acetonitrile solution (Figure 5) of the tetrabutylammonium salt, the ^{31}P NMR line ($\Delta\nu_{1/2}$ = 1 Hz) is flanked by well-resolved satellites (Figure 5a) arising from low-abundance isotopomers containing the only magnetically active ^{183}W isotope[34] ($^2J_{W-P}$ = 18.5 Hz). Integration of the satellites with respect to the central line confirms that the phosphorus atom is surrounded by four equivalent tungsten atoms. In addition the

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^{183}W spectrum (Figure 5b) consists of a well-resolved doublet at −593 ppm ($\Delta\nu_{1/2}$ = 3Hz; $^2J_{W-P}$ = 18.5 Hz). Both observations are in accordance with the persistence in solution of the $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species with the same symmetry properties as in the solid state.[13b] Thus, by NMR spectroscopy (Figure 4) we have clear evidence that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is transferred into the organic phase ($[Q^+]/[PW_{12}O_{40}{}^{3-}] \simeq 3/1$ and 6/1).

The $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ anion was identified by ^{183}W NMR spectroscopy (δ = −697 ppm),[27b] in the aqueous solution before phase transfer, but we were unable to find any signal corresponding to this species in the organic phase with Arquad 2HT (phase-transfer agent).

Raman Spectrometry. The Raman spectra of the peroxo complexes $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in aqueous solution were compared. The spectrum of $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ in the absence of hydrogen peroxide (Figure 6a) has five bands, whose positions coincide with the values found by Griffith et al.[27b] We adopted the assignment proposed for the bands $\bar{\nu}$(W=O) at 962 cm^{-1}, $\bar{\nu}$(O—O) at 853 cm^{-1}, and $\bar{\nu}$(W—OH$_2$) at 326 cm^{-1}, although for the remaining lines our polarization measurements led to the assignment $\bar{\nu}_{as}[W(O_2)]$ at 619 cm^{-1} and $\bar{\nu}_s[W(O_2)]$ at 556 cm^{-1}. The Raman spectrum of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (Figure 6b) was recorded for an aqueous solution containing "H_2WO_4"/H_3PO_4/H_2O_2 (molar ratios 4:1:30), which corresponds to the proportions employed by Venturello et al. to form this complex, subsequently isolated as an onium salt.[13b] Both of these anions have W=O and W(O$_2$) bands and similar Raman spectra (Figure 6). Nevertheless, in the spectrum of $\{PO_4[WO(O_2)_2]_4\}^{3-}$, there is an additional line at 879 cm^{-1} due to the presence of excess hydrogen peroxide. A weak band at 646 cm^{-1} and a very weak band at 1050 cm^{-1} could be attributed to the bridging anion $PO_4{}^{3-}$. It seems difficult to distinguish between $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ from these two lines.

To study the $H_3[PW_{12}O_{40}]/H_2O_2$ interaction, the Raman spectrum of this HPA in aqueous solution (C_W = 0.2 mol L^{-1}) is used as a reference. The spectrum has four strong bands 1014 cm^{-1} (very strong, $\bar{\nu}_s$(W=O$_t$)), 988 cm^{-1} (strong, doublet, $\bar{\nu}_{as}$(W=O$_t$)), and 219 cm^{-1} ($\bar{\nu}_s$(W—O$_\mu$)) attributed according to literature data[35] (O$_t$ = terminal oxygen; O$_\mu$ = oxygen in bridge or μ-oxo). Also seen are bands at 530 and 930 cm^{-1} (Figure 7a).

When a small amount of hydrogen peroxide ($[H_2O_2]/[W]$ = 1) is added to a phosphotungstic acid solution, the Raman spectrum, recorded after the addition (Figure 7b) is different from that of $[PW_{12}O_{40}]^{3-}$. Under these conditions, in a few minutes the solution takes on a yellow color, which is very stable (>6 months at ambient temperature). The strongest Raman line is located at 996 cm^{-1}. There are still weak lines at 220 and 1010 cm^{-1}, which suggests that there is still a small amount of $[PW_{12}O_{40}]^{3-}$. New relatively weak bands appear at 563 and 855 cm^{-1}, which are characteristic of the peroxo structural unit W(O$_2$).

If a slightly larger amount of hydrogen peroxide is added ($[H_2O_2]/[W] \approx$ 3–4), the solution becomes yellow but the color disappears after 1 h. The Raman spectrum recorded in this case is very different from that obtained earlier (Figure 7b): the band at 996 cm^{-1} is no longer as strong and a new peak at 970 cm^{-1} is seen. The overall appearance of this spectrum, like that obtained in the presence of excess hydrogen peroxide, $[H_2O_2]/[W]$ = 15 (Figure 7c), is characteristic of cluster peroxide containing a smaller number of tungsten atoms (Figure 6). The Raman spectra show that $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ are formed.

These results confirm those obtained from the UV study on $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$; for the latter the Raman spectrum in the presence of excess hydrogen peroxide ($[H_2O_2]/[W] \leq 350$) shows that the polyanionic structure is retained without being peroxidized (no band at 830 or 600 cm^{-1}). Furthermore, there are one or more stable peroxo species in a $[PW_{12}O_{40}]^{3-}/H_2O_2$ mixture when $[H_2O_2]/[W] \leq 2$. These anions are probably the intermediates in the degradation process in the presence of excess hydrogen peroxide.[30]

Characterization of Peroxo Complexes Obtained from Excess H_2O_2 and $[PMo_{12}O_{40}]^{3-}$. For the $H_3[PMo_{12}O_{40}]$/excess H_2O_2 system, it is also possible to isolate a peroxo complex containing phosphate (IR: ν_{as}(P–O) at 1070 and 1042 cm^{-1}). In addition, on the basis of elemental analysis, the experimental molar ratios (P/Mo = 0.22; C/Mo = 11.79; N/Mo = 0.76) are compatible with the formula $(Bu_4N)_3\{PO_4[MoO(O_2)_2]_4\}$, similar to that described for the tungsten analogue.[13b] We confirmed that the same peroxo complex can also be obtained from MoO$_3$/excess H_2O_2/H_3PO_4 (see Experimental Section).

Conclusion

Of the polyoxometalates, the precursors that lose their polyanionic structure in the presence of excess hydrogen peroxide are the only ones that lead to an activity similar to that obtained with $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ or $\{PO_4[WO(O_2)_2]_4\}^{3-}$ for the epoxidation of 1-octene under phase-transfer conditions. Various physicochemical methods reveal that these same peroxo complexes are formed from $[PW_{12}O_{40}]^{3-}$ and excess H_2O_2 and that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ is transferred in the organic phase with Arquad 2HT; thus, it is highly likely that this latter heteropolyoxoperoxoanion is at the origin of the catalytic activity.

Experimental Section

Materials. All the polyoxometalates are hydrated compounds. $H_5[BW_{12}O_{40}]\cdot$aq,[36] $H_6[P_2W_{18}O_{62}]\cdot$aq,[37] and $K_4[W_{10}O_{32}]\cdot$aq[38] were prepared by literature procedures.

For all other Mo(VI)- or W(VI)-based precursors, commercial products were used without further purification (Fluka, $H_4[SiW_{12}O_{40}]\cdot$aq, $H_3[PMo_{12}O_{40}]\cdot$aq, and $H_3[PW_{12}O_{40}]\cdot$aq; Eurotungstène, $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot$aq; Prolabo, others). Hydrogen peroxide 30% solutions (Prolabo) were used. 1-Octene (Merck) is better than 97% pure by GC analysis. The phase-transfer agent was a mixture of quaternary ammonium chlorides $\{[(C_{18}H_{37})\ (75\%) + (C_{16}H_{33})\ (25\%)]_2N(CH_3)_2\}^+Cl^-$ marketed by Akzo under the name of Arquad 2HT. It was used after being washed several times with acetone, followed by air drying.

The glass reaction vessel and the NMR tubes were passivated by treatment with a surfactant or with HNO$_3$ 10%/H$_2$O$_2$ 10%.

Spectroscopic Techniques. UV spectra were obtained on Varian DMS 200 apparatus with 1-mm silica cells. Raman spectra were recorded on a Jobin-Yvon U$_{1000}$ spectrometer with a resolution of 4 cm^{-1}. The 514.5-nm exciting line of an Ar$^+$ laser was used, at 300 mW. Solutions of 0.2 M Mo or W of the precursor were studied. IR spectra were measured on a Fourier transform apparatus (Bruker IFS 45) with samples in Nujol suspension between two cesium bromide plates. The ^{31}P NMR spectra were recorded in 10-mm o.d. tubes on a Bruker WM 250, AM500, or MSL 400 apparatus operating at 101.2, 202.4, or 162 MHz, respectively, in the Fourier transform mode. The ^{183}W NMR spectra were recorded on the AM500 and MSL 400 apparatus equipped with a broad-band VSP probehead at 20.8 and 16.6 MHz, respectively; the tungsten NMR spectra were obtained immediately after the phosphorus spectra, on the same solutions, by simply retuning the probehead: the tungsten and phosphorus spectra are then related to the same solution species. The ^{183}W chemical shifts were measured with respect to an external 2 M Na$_2$WO$_4$ solution in alkaline D$_2$O by using saturated dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) in D$_2$O solution as a secondary standard (δ −103.8 ppm), and the ^{31}P chemical shifts are referenced with respect to external 85% H$_3$PO$_4$. The chemical shifts were not corrected for bulk magnetic susceptibility.

Catalytic Tests. Experimental Procedure A = "without Preformation". A 5-mL volume of a CHCl$_3$ solution of the phase-transfer agent (Arquad 2HT, varying amount) was put in a Schlenk tube, followed by the Mo(VI) or W(VI) precursor ($\approx$0.13 mmol of M(VI), in solution or in suspension in water (2 mL)). After the two phases had been vigorously stirred for about 2 min, 1-octene (6.5 mmol) and then 30% hydrogen peroxide (9.8 mmol) were added. The reaction mixture was then stirred at 60 °C (variable reaction time; see Table I).

Experimental Procedure B = "with Preformation". All the 30% hydrogen peroxide (9.8 mmol) was put into a beaker containing the Mo(VI)- or W(VI)-based precursor along with 2 mL of water. After 5 min

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of stirring (necessary for the precursor "to dissolve" completely), the aqueous phase was transferred to a Schlenk tube containing a $CHCl_3$ solution of Arquad 2HT (5 mL). After the two phases were stirred for 2 min, 1-octene (6.5 mmol) was added. The mixture was then stirred under reflux at 60 °C.

Analysis of Reaction Media. At the end of the reaction, the two phases were separated. An aliquot of the aqueous phase was taken and the amount of unreacted H_2O_2 determined by iodometric titration. The organic phase was analyzed by GC with a Girdel apparatus equipped with a 3-m 10% OV 105 on WHP Chromosorb column. 1,2-Epoxyoctane was the major product (internal calibration with anisole). Traces of 1,2-octanediol and heptanal were detected.

Synthesis of Peroxo Complexes. Preparation of $Q_3\{PO_4[WO(O_2)_2]_4\}$ ((a) $Q^+ = (Bu_4N)^+$; (b) $Q^+ = \{[(C_{18}H_{37})$ (75%) + $(C_{16}H_{33})$ (25%)$]_2N(CH_3)_2\}^+$). They are based on the method described by Venturello et al.[13d] Tungstic acid (2.5 g, 10 mmol) was treated with 30% hydrogen peroxide (7 mL, 70 mmol). After 20 min reaction at 50 °C, and then filtration, H_3PO_4 solution (1 mL, 2.5 mmol) was added. The solution was stirred 10 min before isolation of the complex according to one of the following two procedures:

(a) An aqueous solution of $(Bu_4N)^+(HSO_4)^-$ (10 mL, 4 mmol) was slowly added while being stirred. After 10 min, the white precipitate was filtered out, washed thoroughly with water, and then air dried. Anal. Found: C, 30.52; N, 2.40; W, 37.79; P, 2.00. Calcd for $C_{48}H_{108}N_3PW_4O_{24}$: C, 30.70; N, 2.24; W, 39.16; P, 1.65. IR (cm^{-1}): 1086 and 1055 (P—O), 972 (W═O), 855 and 845 (O—O), 595 and 523 ($W(O_2)_{s,as}$); other bands at 730, 650, 575, and 550. Raman spectrum (cm^{-1}, in CH_3CN): 981, 861, 750, 653, 593, 577, 534, 329, 299, and 257.

(b) A solution of Arquad 2HT (3.3 mmol) in 20 mL of $CHCl_3$ was added dropwise to the PO_4^{3-}/"H_2WO_4"/H_2O_2–H_2O system. After 15 min of stirring, the two phases were separated. The organic phase was dried with $MgSO_4$ and the solvent removed on a rotary evaporator. ^{31}P NMR ($CDCl_3$): $\delta = 3.7$ ppm. ^{183}W NMR ($CDCl_3$): $\delta = -590$ ppm.

Preparation of $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$. This preparation was carried out according to the described procedure.[27b] The pH of a solution containing 1 g of potassium tungstate, 30% hydrogen peroxide (7.5 mL), and water (7.5 mL) was adjusted to 2 with HCl (1 M).

White crystals appeared after standing overnight at 5 °C. After 48 h, they were filtered out, washed with ethanol, and air dried. Active oxygen (O_2^{2-}) was determined by iodometric titration: 19.0% (theory 18.6%). IR (cm^{-1}): 964, 850, 835, 775, 617, and 554. Raman (cm^{-1}, aqueous solution): 962, 853, 619, 556, and 326.

Preparations from $H_3[PW_{12}O_{40}]$/Excess H_2O_2. Hydrogen peroxide (30%) (10 mL, 100 mmol) was added to a solution of $H_3[PW_{12}O_{40}]$ (1.65 g or 6 mmol of W in 1 mL of water). After 30 min, an aqueous solution of tetrabutylammonium chloride (1.6 mmol in 3 mL) was slowly added. The resulting white precipitate (I) was filtered out, washed several times with water, and then air dried (yield = 90%). Excess potassium chloride (7 mmol) was added to the recovered filtrate. A few milliliters of ethanol were added to the solution, which was cooled to 5 °C until a snow white precipitate appeared (II). After filtration and washing with ethanol, the precipitate was air dried (yield = 60%).

Analytical data for I are as follows. Anal. Found: C, 31.38; N, 2.31; W, 38.85; P, 1.88. Calcd for $C_{48}H_{108}N_3PW_4O_{24}$: C, 30.70; N, 2.24; W, 39.16; P, 1.65. IR (cm^{-1}): 1084, 1053, 855, 845, 739, 650, 595, 577, 550, and 523. Raman (cm^{-1}): 982, 861, 751, 593, 578, 534, 332, 298, and 257. ^{31}P NMR ($CH_3CN/CDCl_3$): $\delta = 4.2$ ppm (with satellites). ^{183}W NMR ($CH_3CN/CDCl_3$): $\delta = -593$ ppm (doublet, $^2J(W-P) = 18.5$ Hz). Data for the Arquad 2HT salt in $CDCl_3$ are as follows. ^{31}P NMR: $\delta = 3.7$ ppm. ^{183}W NMR: $\delta = -586$ ppm ($\Delta\nu_{1/2} = 80$ Hz).

Analytical data for II are as follows. Active oxygen (O_2^{2-}): 15%. IR (cm^{-1}): 964, 850, 835, 775, 617, and 554.

Preparation from MoO_3/H_3PO_4/Excess H_2O_2. Molybdic oxide (0.9 g, 6.3 mmol) was added to 30% hydrogen peroxide (4 mL, 40 mmol). After reaction (for 1 h at 50 °C) and then filtration, 3 M H_3PO_4 (0.5 mL, 1.5 mmol) was added. After the yellow solution had been stirred for 1 h, an aqueous solution of tetrabutylammonium chloride was slowly added. After 10 min, the yellow precipitate was filtered out, washed thoroughly with water, and air dried. Anal. Found: C, 38.70; N, 2.83; Mo, 25.92; P, 2.18. Calcd for $C_{48}H_{108}N_3PMo_4O_{24}$: C, 37.78; N, 2.75; Mo, 25.15; P, 2.03. IR (cm^{-1}): 1070, 1038, 962, 868, 740, 660, 590, 544, and 517. ^{31}P NMR ($CDCl_3$): $\delta = 7.6$ ppm (Arquad 2HT salt).

Preparation from $H_3[PMo_{12}O_{40}]$/Excess H_2O_2. Hydrogen peroxide (30%) (15 mL, 150 mmol) was added to a solution of $H_3[PMo_{12}O_{40}]$ (1.91 g or 9.8 mmol of Mo in 5 mL of water). After a few minutes of stirring, an insoluble fraction was removed by filtration. The clear yellow solution was left to stand for 15 min before adding slowly an aqueous solution of tetrabutylammonium chloride (2.8 mmol). The resulting yellow precipitate was filtered out, washed thoroughly with water, and air dried. Anal. Found: C, 37.24; N, 2.80; Mo, 25.25; P, 1.80. Calcd for $C_{48}H_{108}N_3PMo_4O_{24}$: C, 37.78; N, 2.75; Mo, 25.15; P, 2.03. IR (cm^{-1}): 1070, 1042, 964, 870, 740, 660, 590, 545, and 520. Raman (cm^{-1}, in CH_3CN): 979, 886, 754, 595, 563, and 529. ^{31}P NMR ($CDCl_3$): $\delta = 7.8$ ppm (salt of Arquad 2HT).

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Registry No. $H_3(PW_{12}O_{40})$, 1343-93-7; $(NH_4)_{10}(H_2W_{12}O_{42})$, 11120-25-5; $(NH_4)_6(Mo_7O_{24})$, 12027-67-7; H_2WO_4, 7783-03-1; Na_2WO_4, 13472-45-2; H_3PO_4, 7664-38-2; $(Bu_4N)_3[PO_4[WO(O_2)_2]_4]$, 92924-16-8; $[(C_{16}H_{33})_2N(CH_3)_2]_3[PO_4[WO(O_2)_2]_4]$, 112399-94-7; $[(C_{18}H_{37})_2N(CH_3)_2]_3[PO_4[WO(O_2)_2]_4]$, 112399-93-6; $K_2[W_2O_3(O_2)_4(H_2O)_2]$, 23298-33-1; ^{183}W, 14265-81-7; 1-octene, 111-66-0.