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Highly Oxidation Resistant Inorganic-Porphyrin Analogue Polyoxometalate Oxidation Catalysts. 2. Catalysis of Olefin Epoxidation and Aliphatic and Aromatic Hydroxylations Starting from α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ ($M^{n+} = Mn^{3+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}), Including Quantitative Comparisons to Metalloporphyrin Catalysts

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Abstract: Several well-characterized transition-metal-substituted polyoxotungstate complexes, α_2-$[(n\text{-}C_4H_9)_4N]_{(11-n)}P_2W_{17}O_{61}(M^{n+}\cdot Br)$ ($P_2W_{17}M$) with M = Mn(III), Fe(III), or Co(II), catalyze the epoxidation of cyclooctene and cyclohexene, with $P_2W_{17}Mn$ performing much better than $P_2W_{17}Fe$ and $P_2W_{17}Co$; the complexes $P_2W_{17}Cu$, $P_2W_{17}Ni$, and P_2W_{18} were almost inactive. $P_2W_{17}Mn$ also catalyzes the oxidation of cyclohexane, adamantane, and heptane, with the formation of the corresponding alcohols and ketones (respective yields around 38, 40, and 5%), as well as the hydroxylation of naphthalene with the formation of 1- and 2-naphthol (43 and 3%). *cis*-Stilbene was epoxidized in a nonstereoselective manner. Many of the characteristics of $P_2W_{17}Mn$-catalyzed oxidations, particularly the regioselectivity of limonene epoxidation and of adamantane and heptane oxidation, are similar to those of the oxidations of the same substrates catalyzed by the hindered Mn–porphyrin Mn(TDCPP)Cl. This suggests a high-valent Mn–oxo intermediate with a difficult substrate access, as the active oxygen species involved in $P_2W_{17}Mn$-catalyzed monooxygenation reactions by PhIO. However, in cyclooctene epoxidations using large excess of PhIO relative to the Mn catalyst, the rates and yields were higher with Mn(TPP)Cl and Mn(TDCPP)Cl than with $P_2W_{17}Mn$.

Introduction

In the preceding paper,[3] we reported the synthesis and characterization of a series of mono-transition-metal-substituted polyoxometalates based on the Dawson framework. These complexes were prepared and characterized with the goal of studying their catalytic atom-transfer chemistry. As a first approach in that direction, we have studied their ability to catalyze the transfer of the oxygen atom of PhIO into various organic substrates. The choice of the oxidant was based on the following reasons. First, the complexes appeared very stable in the presence of an excess of PhIO (see the preceding paper[3]); thus, no metal should be leached during the oxidation reactions. Second, because of the porphyrin-like environment of the heterometal in these complexes involving oxygen atom ligands instead of nitrogen atom ligands in metalloporphyrins (Figure 1), a comparison of their catalytic properties with those of the corresponding metalloporphyrins appeared very important. Moreover, metalloporphyrin-catalyzed oxidations by PhIO have been extensively studied[4] so that the mechanisms of those reactions and the nature of the involved active oxygen species are relatively well known.[4,5]

Some monosubstituted Keggin anions, $[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}(M^{2+})^{4-}$ ($M^{2+} = Mn^{2+}$, Co^{2+}), have been reported to be "remarkably effective catalysts" for the epoxidation of alkenes by PhIO.[6] In order to further characterize the specific reactivity of transition-metal-substituted polyoxotungstate complexes in oxygen atom transfer reactions, we have studied the properties of a series of well-characterized α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ complexes ($M^{n+} = Mn^{3+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}; hereafter denoted $P_2W_{17}M$) as catalysts, not only for alkene epoxidation by PhIO, but also for alkane and arene hydroxylation. The best catalyst determined from these studies, $P_2W_{17}Mn$, was then submitted to more thorough investigations[6b] in comparison to the well-known Mn–porphyrins Mn(TPP)Cl and Mn(TDCPP)Cl under identical conditions.[7] Herein, we report results that allow us to compare directly the catalytic efficiencies of $P_2W_{17}M$ and metalloporphyrins. These results establish the intrinsic properties of the active oxidant involved in $P_2W_{17}Mn$-dependent oxidations, and suggest (but do not prove)[3] that it is a Mn═O species analogous to that proposed for Mn–porphyrins.

Results

Comparative Studies of Cyclooctene Epoxidation by PhIO Using $[(n\text{-}C_4H_9)_4N]^+$ Salts of α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ ($M^{n+} = Mn^{3+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}). The $[(n\text{-}C_4H_9)_4N]^+$ salts of α_2-

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(5) For the active oxygen species formed in Fe– and Mn–porphyrins, see: (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886. (b) Penner-Hahn, J. E.; McMurry, T. J.; Renner, M. W.; Latos-Grazynski, L.; Eble, K. S.; Davis, I. M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Biol. Chem.* **1983**, *258*, 12761-12764. (c) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510-3515. (d) Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628-8638.

(6) (a) Hill, C. L.; Brown, R. B. *J. Am. Chem. Soc.* **1986**, *108*, 536. (b) Besides the claim of remarkably effective catalysts, it is also claimed on p 537 that "the product selectivities, reaction rates, and, most importantly, stabilities for these epoxidations compare favorably with those for all metalloporphyrin and related systems in the literature." The data obtained as part of the present study do not cast the polyoxoanions in quite this favorable a light (not unexpectedly, given that $P_2W_{17}M$ is just the second generation of polyoxoanion catalysts being compared to porphyrins that are the result of a highly evolved and extensive literature). Missing data in the $PW_{11}Mn$ study[6a] include (the lack of) comparisons to the better catalyst Mn(TCDPP)Cl in Tables I-A and I-B, and comparisons to Co–porphyrins of any type in Tables I-C and I-D.

(7) TPP = 5,10,15,20-tetraphenylporphyrin dianion, TMP = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion, TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin dianion.

(8) In the case of α_2-$[(n\text{-}C_4H_9)_4N]_{6.75}H_{0.5}P_2W_{17}O_{61}(Fe\cdot L)$, only a partial ($^1/_4$) equivalent of Br^- is present.[3]

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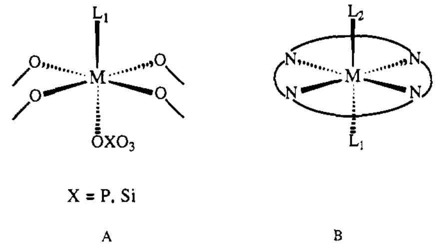

Figure 1. Schematic representations of the coordination spheres of M in (A) $P_2W_{17}M$ and (B) metalloporphyrin complexes.

Table I. Epoxidation of Cyclooctene by PhIO Catalyzed by Various Transition-Metal-Substituted Polyoxotungstate Complexes[a]

	yield (%)	
catalyst	epoxide	PhI
$P_2W_{17}Mn(III)^b$	88	100
$PW_{11}Mn(II)$	85	97
$P_2W_{17}Fe(III)$	87	90
$P_2W_{17}Co(II)$	68	85
$P_2W_{17}Ni(II)$	2	
$P_2W_{17}Cu(II)$	2	
$P_2W_{18}{}^c$	<1	
$PW_{12}{}^d$	<1	

[a] Conditions: catalyst (2.2×10^{-3} M in CH_3CN/CH_2Cl_2, 1:1): PhIO:cyclooctene = 1:10:500 (molar ratio). Yields of cyclooctene oxide and PhI obtained after 2 h at 20 °C are based upon starting PhIO. [b] Because $P_2W_{17}Mn$ contains 1 equiv of Br^- [α_2-$P_2W_{17}O_{61}(Mn{\cdot}Br)^{8-}$], a control was done to see if 1 equiv of added [$(n$-$C_4H_9)_4N$]Br influenced the results. It did not in a control reaction with $P_2W_{17}Mn$:PhIO:cyclooctene:[$(n$-$C_4H_9)_4N$]Br = 1:10:500:1. Similar controls, under the standard 1:10:500 conditions, showed that 1 equiv of HBr, CF_3CO_2H, or CH_3CO_2H also had no effect on the rates or yields of cyclooctene epoxidation. [c] P_2W_{18} = [$(n$-$C_4H_9)_4N]_6P_2W_{18}O_{62}$. [d] PW_{12} = [$(n$-$C_4H_9)_4N]_3PW_{12}O_{40}$.

$P_2W_{17}O_{61}(M^{n+}{\cdot}Br)^{(n-11)}$ (hereafter "$P_2W_{17}M$") were investigated for their relative abilities to catalyze the epoxidation of cyclooctene by PhIO at room temperature. In experiments using a catalyst:PhIO:cyclooctene molar ratio of 1:10:500 and a CH_3CN/CH_2Cl_2 (1:1) solvent mixture, epoxidation yields around 90% were obtained within 1 h at 20 °C with $P_2W_{17}Mn(III)$ and $P_2W_{17}Fe(III)$ as catalysts. The previously reported [$(n$-$C_4H_9)_4N]_4H$-[$PW_{11}Mn(II)O_{39}]^{5-}$ catalyst, $PW_{11}Mn(II)$, gave identical yields. $P_2W_{17}Co(II)$ led to lower yields (around 70%), whereas all the other studied compounds, $P_2W_{17}Ni(II)$ and $P_2W_{17}Cu(II)$, as well as the reference polyoxotungstate complexes without a low-valent metal P_2W_{18} ([$(n$-$C_4H_9)_4N]_6P_2W_{18}O_{62}$) and PW_{12} ([$(n$-$C_4H_9)_4N]_3PW_{12}O_{40}$) were almost inactive under identical conditions (Table I). Therefore, in the following, we have studied in detail only the oxidations catalyzed by the more interesting polyoxometalate catalysts $P_2W_{17}Mn(III)$ and $P_2W_{17}Fe(III)$.

Cyclohexene Oxidation by PhIO Catalyzed by $P_2W_{17}Mn(III)$ and $P_2W_{17}Fe(III)$: Comparison with Mn(III)- and Fe(III)-Porphyrins as Catalysts. Table II shows that $P_2W_{17}Mn(III)$ gave very similar results as the three Mn(III) porphyrins Mn(TPP)Cl, Mn(TMP)Cl, and Mn(TDCPP)Cl[7] as catalysts for cyclohexene oxidation by PhIO under anaerobic conditions. Both types of catalysts led to cyclohexene epoxide as a major product (yields around 70%) and to the corresponding allylic alcohol as a minor product (yields around 5%). As far as iron(III) catalysts are concerned, the iron–porphyrin Fe(TDCPP)Cl led to an almost quantitative oxygen atom transfer to cyclohexene with a 96% epoxidation yield, whereas $P_2W_{17}Fe(III)$ was a very poor catalyst (16% total yield). Under identical conditions, control experiments with P_2W_{18} and PW_{12} showed that they did not catalyze cyclohexene epoxidation and instead gave only low yields of allylic oxidation products. With all of the Fe(III) and Mn(III) catalysts tested for cyclohexene oxidation, yields of PhI were close to 100% except for $P_2W_{17}Fe(III)$ for which a 82% yield was obtained. With this catalyst, PhIO disproportionation to $PhIO_2$ and PhI was observed.

Table II. Oxidation of Cyclohexene by PhIO Catalyzed by Polyoxotungstate or Metalloporphyrin Complexes[a]

	yield (%)			
catalyst	epoxide	allylic alcohol	allylic ketone	PhI
$P_2W_{17}Mn(III)$	69	3	2	100
Mn(TPP)Cl	58	7	1	100
Mn(TMP)Cl	75	5	1	100
Mn(TDCPP)Cl	84	5	1	100
$P_2W_{17}Fe(III)$	13	3	<1	82
Fe(TDCPP)Cl	96	3	<1	100
P_2W_{18}	1	2	<1	

[a] Conditions as in Table I except that all experiments were done under anaerobic conditions (under argon) to avoid cyclohexene autoxidation.

Table III. Compared Characteristics of *cis*-Stilbene and (+)-Limonene Epoxidation Catalyzed Either by $P_2W_{17}Mn$ or by Mn(III)-Porphyrins[a]

alkene	catalyst	total epoxide yield (%)	epoxide ratio
cis-stilbene, (PhCH=CHPh)	$P_2W_{17}Mn$	48	*cis*:*trans* = 55:45
	Mn(TPP)Cl	90	*cis*:*trans* = 39:61
	Mn(TDCPP)Cl	96	*cis*:*trans* = 96:4
(+)-limonene[b]	$P_2W_{17}Mn$	75	1,2-:8,9-oxide = 2.4[b]
	Mn(TPP)Cl	54	1,2-:8,9-oxide = 7.5[b]
	Mn(TDCPP)Cl	71	1,2-:8,9-oxide = 1.3[b]

[a] Conditions as in Table I. Yields of *cis*- and *trans*-stilbene oxide were determined by ^1H NMR spectroscopy as previously described.[9a] [b] (+)-Limonene oxidation was studied by GC as reported previously.[9a] Limonene 1,2-oxide was found as a mixture of cis and trans isomers and limonene 8,9-oxide as a mixture of two diastereoisomers.[9a] See Figure 2.

From the results obtained for cyclooctene and cyclohexene oxidation, $P_2W_{17}Mn$ appeared to be the best polyoxometalate catalyst. In the following, it was studied in more detail and compared with the Mn–porphyrins Mn(TPP)Cl and Mn(TDCPP)Cl.

Epoxidation of Alkenes by PhIO: Comparison between $P_2W_{17}Mn$ and Mn–Porphyrins as Catalysts. The active oxygen species involved in monooxygenations of hydrocarbons by PhIO catalyzed by Mn(III)–porphyrins is thought to be a high-valent Mn=O species (formally a Mn(V)=O complex) with a marked free radical character.[5c,d] The stereochemistry and regioselectivity of Mn–porphyrin reactions with alkenes are found to be very dependent upon the presence of bulky substituents in ortho positions of the *meso*-aryl groups of the porphyrin.[9] As shown in Table III, Mn(TDCPP)Cl led to an almost stereoselective epoxidation of *cis*-stilbene (*cis*:*trans*-epoxide = 96:4) corresponding to a syn addition of the oxygen atom of PhIO to the double bond, whereas the less bulky Mn(TPP)Cl led to a nonstereoselective epoxidation with a slightly preferred formation of the *trans*-epoxide.[10] This was interpreted as due to a free radical intermediate formed upon addition of the Mn(IV)–O• species to the double bond, followed by a more or less facile rotation around this intermediate's C–C bond as a function of the steric hindrance of the ortho substituents of the porphyrin *meso*-aryl groups.[9] Under identical conditions, $P_2W_{17}Mn$ led to a 50% yield of *cis*-stilbene epoxidation with a *cis*:*trans*-epoxide ratio intermediate between those obtained with Mn(TPP)Cl and Mn(TDCPP)Cl, but closer to that obtained with Mn(TPP)Cl.

No significant isomerization of *cis*-stilbene to *trans*-stilbene occurred during the reaction. In fact, *trans*-stilbene alone was epoxidized by PhIO in the presence of $P_2W_{17}Mn$ under identical conditions but only gave a relatively low yield (8%) of *trans*-

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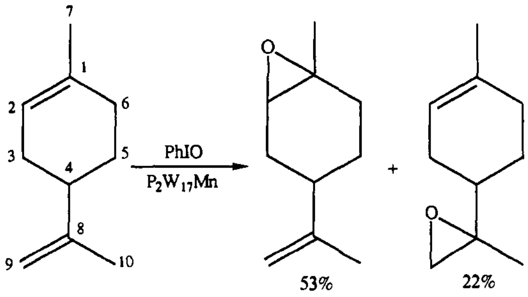

Figure 2. P_2W_{17}Mn-catalyzed epoxidation of (+)-limonene by PhIO.

stilbene epoxide. However, the oxidation of a 1:1 mixture of *cis*- and *trans*-stilbene (conditions:*cis*-stilbene:*trans*-stilbene:PhIO = 1:1:1) led to an almost exclusive consumption of *cis*-stilbene (40% consumed) and the formation of a mixture of *cis*- and *trans*-epoxides with a 55:45 ratio identical with that observed with *cis*-stilbene alone. Furthermore, the amounts of *trans*-stilbene (3%) present as an impurity in commercial *cis*-stilbene were found unchanged at the end of the reaction. Thus, the order of reactivity of stilbenes (*cis*-stilbene > *trans*-stilbene) observed for the active species derived from P_2W_{17}Mn is the same as that previously reported for the active species derived from Mn(III)–porphyrins.[4]

The above data show that the 55:45 *cis*:*trans*-epoxide ratio obtained in the P_2W_{17}-catalyzed epoxidation of *cis*-stilbene is really linked to the intrinsic stereochemistry of *cis*-stilbene epoxidation by P_2W_{17}Mn and not to *cis*-stilbene isomerization and epoxidation of the resulting *trans*-stilbene. Interestingly, this P_2W_{17}Mn-catalyzed oxidation of *cis*-stilbene by PhIO gave the corresponding epoxides as main products and minor amounts of $PhCOCH_2Ph$ (3%) but no formation of benzaldehyde. In comparison, the oxidation of *cis*-stilbene by PhIO catalyzed by Mn(III) triflate was reported to give large amounts of PhCHO.[11] [Hill's work[6] documents that the simple salts $Mn(OTf)_3$ and $Co(OTf)_2$ are less effective catalysts than the polyoxoanion-bound metals. Hence, we have not reexamined simple salts like $Mn(OTf)_3$.]

The regioselectivity of (+)-limonene epoxidation catalyzed by Mn–porphyrins, that is, the ratio between 1,2-epoxide and 8,9-epoxide (Figure 2), is known to be very sensitive to any hindrance to Mn access in the porphyrin series.[9a] In the case of P_2W_{17}Mn, Table III shows that the regioselectivity of (+)-limonene epoxidation is intermediate between those observed with Mn(TDCPP)Cl and Mn(TPP)Cl, but closer to that of Mn(TDCPP)Cl. It is noteworthy that the regioselectivities observed with P_2W_{17}Mn and Mn(TDCPP)Cl were not greatly modified when the reaction temperature was changed from 20 to 0 °C (1,2-epoxide:8,9-epoxide ratio varying from 1.3 to 1.1 for Mn(TDCPP)Cl and from 2.4 to 2.0 for P_2W_{17}Mn).

All the experiments described above were performed with a moderate excess of PhIO relative to the catalyst (catalyst:PhIO:substrate = 1:10:500). In order to compare the catalytic activity of P_2W_{17}Mn and Mn–porphyrins, more catalytic conditions (lower catalyst concentration) were used, catalyst:PhIO:cyclooctene = $1:10^3:10^5$, with a catalyst concentration of 10^{-5} M. We have checked that, under these conditions, the initial rates of P_2W_{17}Mn-catalyzed epoxidation of cyclooctene by PhIO were almost linearly dependent on the catalyst concentration (at least for catalyst concentrations between 5×10^{-6} and 5×10^{-5} M); that is, the rate-determining step does involve the P_2W_{17}Mn catalyst. As shown in Figure 3, with Mn(TDCPP)Cl as catalyst, the 1000 equiv of PhIO were consumed within less than 1 h with an almost quantitative formation of cyclooctene oxide and PhI. A further addition of PhIO led to identical yields and rates. Very similar results were observed with Mn(TPP)Cl except that the epoxide yield was only 80% and that the rate of PhIO consumption was slightly lower. P_2W_{17}Mn gave substantially lower epoxidation yields (around 40%) and much lower rates. The initial activity of Mn(TDCPP)Cl was about 1200 turnovers per hour, whereas that of P_2W_{17}Mn was 60-fold lower, only about 20 turnovers per hour.

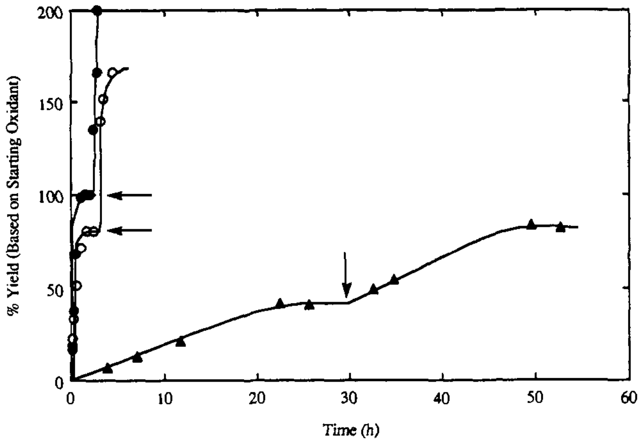

Figure 3. Kinetics of cyclooctene epoxidation by PhIO catalyzed by either P_2W_{17}Mn(III) or by Mn(III)-porphyrins. Conditions: Addition of 1000 equiv of PhIO to a solution of 10^{-5} M catalyst and 1 M cyclooctene in CH_3CN/CH_2Cl_2 at 17 °C. Arrows indicate a second addition of 1000 equiv of PhIO to the reaction mixture. Key: ▲, P_2W_{17}Mn; ●, Mn(TDCPP)Cl; ○, Mn(TPP)Cl.

Table IV. Oxidation of Cyclohexane by PhIO Catalyzed by Various Transition-Metal-Substituted Polyoxotungstate Complexes[a]

	product yield (%)		
catalyst	cyclohexanol	cyclohexanone	PhI
P_2W_{17}Mn(III)	16	11	90
PW_{11}Mn(II)	27	19	82
P_2W_{17}Co(II)	4	2	77
P_2W_{17}Ni(II)	1	1	
P_2W_{17}Cu(II)	1	1	
P_2W_{18}	<1	1	

[a] Conditions as in Table I except for the catalyst:PhIO:substrate molar ratio = 1:20:2000. Yields based on starting PhIO were maximum after 2 h at 20 °C except for P_2W_{17}Ni and P_2W_{17}Cu for which oxidation yields around 10% were obtained after 72 h.

It is noteworthy that both of the Mn–porphyrins and P_2W_{17}Mn were stable under the conditions employed (catalyst:PhIO:cyclooctene = $1:10^3:10^5$) as demonstrated by the fact that the further addition of 1000 equiv of PhIO gave identical rates and yields (Figure 3). Furthermore, we demonstrated that Mn(TDCPP)Cl was able to perform 100 000 turnovers, with successive additions of 1000 equiv of PhIO, without appreciable degradation of the catalyst under these conditions. Unfortunately, it was not possible to do similar experiments due to the 60-fold slower kinetics obtained with P_2W_{17}Mn. (In the case of PW_{11}Mn, a claim of 10 000 turnovers has appeared, but no details are available.[6])

In order to compare further the stability of the porphyrin and polyoxoanion Mn catalysts in the presence of PhIO, identical experiments *without cyclooctene* were performed. (In the absence of cyclooctene, which efficiently captures the active species, one would expect a faster autodestruction of the catalyst.) After 24 h at 20 °C in the presence of 1000 equiv of PhIO in CH_3CN/CH_2Cl_2 (1:1), Mn(TPP)Cl *and* Mn(TDCPP)Cl (10^{-5} M) underwent a 65% and 50% destruction, respectively, as measured by UV–visible spectroscopy. In contrast, under identical conditions, P_2W_{17}Mn was found intact within experimental error. The lack of decomposition of the P_2W_{17}Mn catalyst was demonstrated by adding cyclooctene to the reaction mixture, which led to epoxidation rates and yields that were identical with those observed without waiting for 24 h before cyclooctene addition. This has been confirmed by quantitative IR measurements of the polyoxometalate-framework absorbances before and after the addition of 1500 equiv of PhIO (no added cyclooctene).[3] Clearly, the polyoxometalate is a rather robust oxidation catalyst! This is significant since a recent study[12] has concluded that even the

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Table V. Comparison of the Oxidation of Adamantane and Heptane by PhIO Catalyzed by $P_2W_{17}Mn(III)$ and Mn(III)–Porphyrins[a]

alkane	catalyst	total yield of oxidation products (%)	regioselectivity (alcohol or ketone)		
			1-ol	2-ol	2-one
adamantane	$P_2W_{17}Mn$	40	28	6	3
	Mn(TPP)Cl	57	42	9	3
	Mn(TDCPP)Cl	43	28	10	2.5

alkane	catalyst	total yield of oxidation products (%)	regioselectivity (alcohol + ketone)[b]			
			1	2	3	4
heptane[b]	$P_2W_{17}Mn$	5	2	55	35	8
	Mn(TPP)Cl	20	<1	39	41	20
	Mn(TDCPP)Cl	30	4	58	27	11

[a] Conditions as in Table IV, except for adamantane for which a Mn:PhIO:alkane = 1:10:250 ratio in CH_3CN/CH_2Cl_2 (1:4) was used because of solubility problems. Total yields based on starting PhIO were calculated assuming that 2 mol of PhIO were necessary for the formation of 1 mol of ketone. [b] Percentages of products (alcohol + ketone) coming from the oxidations of positions 1, 2, 3, or 4 of heptane.

stabilized tetrakis(pentafluorophenyl)porphyrins "are still too fragile for prolonged alkane oxidation at elevated temperatures." (The presence of organic Bu_4N^+ counterions is one possible limit to the polyoxoanion catalyst's long-term stability during difficult or slow oxidation reactions.)

Oxidation of Alkanes by PhIO Catalyzed by $P_2W_{17}Mn$. $P_2W_{17}Mn$ catalyzed the oxidation of cyclohexane by PhIO with the formation of cyclohexanol (16%) and cyclohexanone (11%) (Table IV). With a catalyst:PhIO:cyclohexane ratio of 1:10:500, PhIO consumption was complete within less than 2 h at 20 °C and led to high yields of PhI. $PW_{11}Mn$ gave similar results but slightly higher alcohol and ketone yields. $P_2W_{17}Co$ was much less active, and $P_2W_{17}Ni$, $P_2W_{17}Cu$, and P_2W_{18} gave yields lower than 1% after 2 h. However, it is noteworthy that $P_2W_{17}Ni$ and $P_2W_{17}Cu$ led to moderate but significant yields of cyclohexanol and cyclohexanone *after 24 h* under identical conditions.

Table V compares the results obtained for the oxidation of various alkanes by PhIO catalyzed either by $P_2W_{17}Mn$ or Mn(TDCPP)Cl. With cyclohexane, similar alcohol:ketone ratios were obtained with both catalysts, though Mn(TDCPP)Cl gave better yields. Both catalysts gave very similar results for adamantane oxidation with a large preference for the hydroxylation of tertiary C–H bonds. $P_2W_{17}Mn$ was a poor catalyst for heptane oxidation by PhIO (total yield of about 5%). Interestingly, the regioselectivity of heptane oxidation was intermediate between that obtained with the unhindered Mn(TPP)Cl, which is typical for a statistical attack of the three types of secondary hydrogen atoms (around 40:40:20 for positions 2, 3, and 4), and that observed with Mn(TDCPP)Cl, for which oxidation on the more accessible position 2 is favored because of a difficult access of heptane to the hindered active species[9a] (61:28:11 for positions 2, 3, and 4).

Discussion

The aforementioned data confirm that some transition-metal-substituted heteropolytungstate complexes do catalyze alkene epoxidation by PhIO. They also show that those complexes catalyze the oxidation of various alkanes into the corresponding alcohols and ketones under mild conditions. For both kinds of reactions, $P_2W_{17}Mn(III)$ is the superior catalyst compared to either $P_2W_{17}Fe(III)$ or $P_2W_{17}Co(II)$. As monooxygenation catalysts, the polyoxotungstates exhibit the following order of efficacy:

$$P_2W_{17}Mn \gg P_2W_{17}Fe > P_2W_{17}Co \gg P_2W_{17}Cu \approx P_2W_{17}Ni \gg P_2W_{18}$$

Also noteworthy is that $P_2W_{17}Mn(III)$ exhibits a behavior very similar to that of $PW_{11}Mn(II)$; the latter is presumably[6] oxidized to $PW_{11}Mn(III)$ under the reaction conditions.

Table VI. Comparison of the Characteristics of the Oxidations Catalyzed by $P_2W_{17}Mn$ and Mn(III)–Porphyins[a]

	$P_2W_{17}Mn$	Mn(TDCPP)Cl	Mn(TPP)Cl
cis-stilbene, *cis*:*trans*-epoxide ratio	1.2	24	0.7
(+)-limonene, 1,2-:8,9-epoxide ratio	2.4	1.3	7.5
adamantane, regioselectivity (1:2 position)	3.1	2.3	3.5
heptane, 2:3:4 position (%)	57:35:8	61:28:11	39:41:20
naphthalene,[b] 1- and 2-naphthol yields	43:3	22:2	<1
competition[c], cyclooctene + cyclohexane, epoxide:ol + one	16	12	7

[a] Results concerning *cis*-stilbene, limonene, adamantane, and heptane were derived from Tables III and V. [b] Conditions used for naphthalene oxidation were those indicated in Table I. [c] Competition between cyclooctene and cyclohexane was studied under the following conditions: Mn:PhIO:cyclooctene:cyclohexane = 1:10:50:450 with the catalyst 2.2 mM in CH_3CN/CH_2Cl_2 (1:1). Yields were determined after 2 h at 20 °C, and the indicated figures are the cyclooctene oxide:cyclohexanol + cyclohexanone ratios.

The oxygen active species involved in $P_2W_{17}Mn$-catalyzed oxidations exhibit several characteristics similar to those involved in Mn(III)–porphyrin-catalyzed oxidations. Both the polyoxoanion and porphyrin catalysts epoxidize alkenes, both are not completely stereoselective in the case of *cis*-stilbene, and both oxidize alkanes with formation of similar amounts of alcohols and ketones and with a marked preference for tertiary C–H bond hydroxylation in the case of adamantane. Both catalysts also hydroxylate naphthalene with preference for the formation of 1-naphthol (Table VI). Moreover, in competition experiments between cyclooctene and cyclohexane (catalyst:PhIO:cyclooctene:cyclohexane = 1:10:50:450), $P_2W_{17}Mn$ and Mn(TDCPP)Cl led mainly to cyclooctene epoxide (respective cyclooctene epoxide:cyclohexanol + cyclohexanone ratios of 16 and 12) (Table V), indicating that the active species derived from both catalysts are much more reactive toward double bonds than toward alkane C–H bonds, as expected.

Since it is generally believed that high-valent Mn=O intermediates (formally Mn(V)=O species) are involved in alkene epoxidations and alkane hydroxylations catalyzed by Mn(III)–porpyrins,[5c,d] it is certainly possible (but unproven)[11b] that similar active oxygen species are involved in $P_2W_{17}Mn$-dependent oxidations.[13] A comparison of the regioselectivities of the epoxidation of (+)-limonene and of the hydroxylation of adamantane and heptane, catalyzed either by $P_2W_{17}Mn$ or by more or less hindered Mn–porphyrins, should give an idea of the accessibility of substrates toward the active oxidant. In fact, the regioselectivities observed for $P_2W_{17}Mn$ with each of these substrates are always intermediate between those observed for the unhindered Mn(TPP)Cl catalyst and for the more bulky Mn(TDCPP)Cl (Table VI). Overall, the regioselectivities were closer to those observed

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(13) In part in response to a reviewer's query, it is useful to summarize the following seven lines of evidence that argue strongly that, *in the present example*, the active catalyst is indeed Mn incorporated into the $P_2W_{17}O_{61}{}^{10-}$ framework and not free $Mn^{n+}(solvent)_x$: (1) The binding K_{eq} for Mn^{3+} to $P_2W_{17}O_{61}{}^{10-}$ is 10^5 in H_2O, and probably several powers of 10 greater than this in organic solvents.[3] (2) IR controls[3] confirm that all the $P_2W_{17}Mn$ remains intact within experimental error following treatment with PhIO for 48 h. (3) The rate of cyclooctene epoxidation after $P_2W_{17}Mn$ treatment with PhIO for 24 h is identical with the initial rate before any such treatment. (4) The rates of $P_2W_{17}Mn$ epoxidation of cyclooctene by PhIO are linear, Figure 3 (until the end where the PhIO is nearly all gone), and are first-order in catalyst over a 10-fold concentration range (see the section on "Epoxidation of Alkenes..."). This data plus that in (1), (2), and (3) would require a mechanistic postulate that only a trace amount of dissociated, free Mn^{3+} is the actual catalyst, but this can be ruled out by the data in (5). (5) The literature[6a] indicates that free Mn^{3+} ($Mn(OTf)_3$) is an inferior (slower) catalyst relative to $PW_{11}Mn$ (and our data show that $PW_{11}Mn$ and $P_2W_{17}Mn$ are roughly comparable catalysts). (6) The data herein show that different products (i.e., no PhCHO) are seen for $P_2W_{17}Mn$ in comparison to free Mn^{3+}. (7) The $P_2W_{17}Mn$ data presented herein exhibit regio- and stereoselectivities which mimic those of a somewhat hindered metalloporphyrin, not those of a relatively unhindered, solvated Mn^{3+} ion.

in Mn(TDCPP)Cl-catalyzed oxidations. This would suggest a Mn active species with a somewhat hindered substrate approach in $P_2W_{17}Mn$. This may be due to the steric influence of peripheral oxygen atoms or the steric effect of ion-paired, bulky $[(n\text{-}C_4H_9)_4N]^+$ ions.

Summary

In $\alpha_2\text{-}P_2W_{17}O_{61}(Mn)^{7-}$, the Mn active site is ligated by four planar polyoxoanion oxygens (and one axial $O\text{-}PO_3$ oxygen) similar to how Mn(III) is firmly bound to four planar nitrogen atoms of a porphyrin ring (plus any axial ligands). Both the $P_2W_{17}Mn$ polyoxometalate and Mn–porphyrin catalysts exhibit similar properties for the catalysis of oxygen atom transfer from PhIO. The anticipated stability of the polyoxometalate catalysts in the presence of strong oxidizing agents was confirmed in the presence of excess PhIO, even in the absence of a reactive olefin or other substrates. In that regard, Mn–polyoxotungstate complexes are superior to the Mn–porphyrins examined herein.[6] However, $P_2W_{17}Mn(III)$ was found to give lower rates and yields in cyclooctene epoxidation using large excess of PhIO (relative to Mn) than Mn(TDCPP)Cl and even than Mn(TPP)Cl; in this regard, the polyoxoanions are somewhat less effective catalysts than previously implied.[6] Hence, a crucial point is that more active and efficient polyoxometalate catalysts are desirable.

It is worth noting that, in many ways, polyoxoanions (and their $E_{1/2}$ values, for example) are more readily modified than metalloporphyrins (for example, by substitution of one or more other metals for W in the framework). Hence, we anticipate that third, fourth, and even later generations of such polyoxoanion catalysts will prove possible, limited only by the difficulties[3] in synthesizing and fully characterizing the needed materials. Providing such catalysts is one of our future research goals.

Experimental Section

Physical Measurements. UV–vis spectra were recorded on an Aminco DW 2A spectrophotometer. Gas chromatography analysis was done with an Intersmat I.G. 120 FL chromatograph equipped with a hydrogen flame ionization detector. The glass column (length 3 m, internal diameter 3 mm) was packed with 5% or 10% FFAP on chromosorb (WAW 80/100 mesh) for aliphatic epoxides, alcohols, ketones, and naphthols and with carbowax 20M 5% for stilbene oxide. The limonene oxidation products were studied on a Girdel (N°11828) apparatus equipped with a SE-32 capillary column (50 m × 0.32 mm). The products formed were analyzed by comparison of their retention time with those of authentic samples and by gas chromatography–mass spectroscopy (GC–MS) coupling analysis. Yields were determined by using internal standard methods. Mass-gas chromatography coupling analyses were performed on a Ribermag apparatus. ^1H NMR spectra were recorded at 20 °C in $CDCl_3$ on a Brucker WM 250 spectrometer operating at 250 MHz.

Materials. Acetonitrile and dichloromethane, HPLC grade (S.D.S. Vitry, France), were used as received. All alkene, alkane, and aromatic substrates were purchased in their highest commercial purity, stored at 5 °C, and purified just before use. Cyclohexene oxide, cyclooctene oxide, and (+)-1,2-limonene oxide were purchased from Janssen and *trans*-stilbene oxide from Aldrich. (+)-8,9-Limonene oxide was prepared by the peroxybenzimidic acid method,[14] and trans-1,2-limonene oxide was prepared by the hydrolysis of the commercial 1,2-epoxide, tosylation of the resulting diol, and cyclization by methanolic KOH.[15] Iodosylbenzene was prepared by hydrolysis of iodobenzene dichloride with aqueous NaOH[16] carefully dried under reduced pressure and kept at 5 °C.

Polyoxometalate Catalysts. The monosubstituted polyoxometalates $P_2W_{17}M$ used in the study were prepared and characterized as detailed in the preceding paper.[3] $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_6P_2W_{18}O_{62}$ and $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PW_{12}O_{40}$ were prepared by the metathesis of $\alpha\text{-}K_6P_2W_{18}O_{62}$, prepared according to the literature,[17] and $\alpha\text{-}H_3PW_{12}O_{40}$ (Fisher) with $[(n\text{-}C_4H_9)_4N]Br$ (Fluka). Both compounds were twice recrystallized from 60 °C CH_3CN, air-dried on a glass frit, and determined to be more than 99% pure by C, H, and N elemental analysis and ^{31}P NMR. (The ^{31}P NMR methods are described in ref 3.)

Mn–Porphyrins. *meso*-Tetraphenylporphyrin ($TPPH_2$) was prepared according to Adler et al.[18] and the chlorin impurity removed by the method described by Smith et al.[19] *meso*-Tetrakis(2,4,6-trimethylphenyl)porphyrin ($TMPH_2$) and *meso*-tetrakis(2,6-dichlorophenyl)porphyrin ($TDCPPH_2$) were obtained by the method of Lindsey and Wagner[20] with modifications similar to those recently published.[21] Insertion of Mn was done by conventional methods.[22]

Typical Oxidation Procedure and Product Analysis. Most reactions were carried out in a 5-mL tube equipped with a serum cap and a stirring bar. Catalysts and substrates were dissolved in a CH_2Cl_2/CH_3CN (generally 1:1) mixture. PhIO was then added. For reactions done under argon, the reaction mixture was purged by three freeze–thaw cycles. GLC analysis was performed on aliquots withdrawn directly from the reaction mixture. Typically, PhIO (10 μmol) was added to a CH_2Cl_2/CH_3CN solution (0.2:0.2 mL) of the catalyst (1 μmol) and of the substrate (0.5 mmol). After stirring 2 h at ambient temperature, the internal standard was added and the reaction mixture analyzed by GLC. In most cases, reactions were achieved in about 1 h under those conditions. Identical yields were obtained after 24 h.

Kinetics of Cyclooctene Epoxidation by PhIO Catalyzed by Either $P_2W_{17}Mn$ or Mn(III)–Porphyrins. To a 10 μM solution of catalyst in a CH_2Cl_2/CH_3CN (1:1) mixture containing 1 M cyclooctene, 1000 equiv (relative to the catalyst) of PhIO was added. Aliquots were withdrawn and poured into a sodium thiosulfate solution in order to destroy the excess PhIO, and the organic phase was analyzed by GLC.

Measurement of Mn–Porphyrin Destruction by PhIO. Conditions identical with those described above for the kinetics of cyclooctene epoxidation by PhIO were used but without cyclooctene. 300 μL of the solution were withdrawn after 24 h reaction at 20 °C and studied by UV–vis spectroscopy (350–550 nm). The obtained spectrum of the Mn(III)–porphyrin was almost identical with that of the starting solution ($t = 0$, before addition of PhIO) but much less intense, indicating that a part of the Mn–porphyrin catalyst was destroyed without appearance of any new species absorbing between 350 and 550 nm. The observed decrease of the Soret peak after 24 h reaction was 65% for Mn(TPP)Cl and 50% for Mn(TDCPP)Cl.

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Registry No. $P_2W_{17}Mn$, 135224-89-4; $P_2W_{17}Fe$, 135224-88-3; $P_2W_{17}Co$, 135224-87-2; Mn(TPP)Cl, 32195-55-4; Mn(TDCPP)Cl, 91463-17-1; cyclohexene, 110-83-8; cyclooctene, 931-88-4; *cis*-stilbene, 645-49-8; (+)-limonene, 5989-27-5; *cis*-stilbene oxide, 1689-71-0; cyclohexane, 110-82-7; adamantane, 281-23-2; heptane, 142-82-5.

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