Selective Homogeneous Catalytic Epoxidation of Alkenes by Hydrogen Peroxide Catalysed by Oxidatively- and Solvolytically-resistant Polyoxometalate Complexes

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The d-election transition metal-substituted heteropolytungstate sandwich complex $[(Fe^{II})_4(B\text{–}PW_9O_{34})_2]^{10-}$, unlike $PW_{12}O_{40}^{3-}$ and most polytungstophosphates, is quite stable with respect to solvolysis by H_2O_2 and catalyses the selective homogeneous epoxidation of alkenes in aqueous acetonitrile at 20 °C by this oxidant.

New and effective catalytic methodologies for the selective oxidation of hydrocarbons by O_2 or H_2O_2 are of particular interest given the growing concern for the deleterious environmental impact of halocarbon solvents and/or halogenated oxidants.[1–4] In this context, two of the most discussed and examined systems involving the selective catalytic oxidation by H_2O_2 are the homogeneous epoxidation systems reported by Venturello and co-workers[5] and Ishii and co-workers.[6] Although the precursors and some of the features of these two systems are different (Venturello system: WO_4^{2-}, PO_4^{3-} and H_2O_2 in H_2O/alkene substrate in chlorocarbon/phase-transfer agent; Ishii system: $PW_{12}O_{40}^{3-}/H_2O_2$ in H_2O/alkene substrate in chlorocarbon/phase transfer agent), other features are the same or very similar: the observed high selectivities for epoxide at high alkene conversion and the intermediacy of at least one peroxo complex, that isolated by Venturello in 1985, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$.[7] Two major impediments to the further commercial development of the Venturello and Ishii chemistry is that it functions well only in chlorinated solvents and is subject to catalyst deactivation. We report here that the heteropolytungstate sandwich complex $[(Fe^{II})_4(B\text{–}PW_9O_{34})_2]^{10-}$, **1**, catalyses the selective epoxidation of alkenes by H_2O_2 and addresses both of the above limitations. Furthermore, this is the first report in the literature that demonstrates that a polyoxometalate can have substantial stability with respect to degradation in protic media containing hydrogen peroxide (hydrolytic and peroxylytic stability) while exhibiting catalytic activity for substrate oxidation. This catalyst also shares in common with methane monooxygenase and other enzymes, and with biomimetic systems thereof,[8] a redox functional polyiron active site. In recent years, several non-porphyrin iron-containing catalysts of hydrocarbon oxidation by peroxides have been reported,[1–3] but only a few of these are reported to catalyse the epoxidation of olefins with high selectivity.[9]

The deca-potassium salt of **1**, **K1**, was prepared by the procedure used by Finke *et al.* for the corresponding Co, Cu and Zn derivatives,[10] and the tetra-*n*-butylammonium (^4Q) salt of **1**, $^4Q_{10}[(Fe^{II})_4(B\text{–}PW_9O_{34})_2]$ or ^{4}**Q1**, was prepared by mixing **K1** and ^{4}QBr in water at pH = 7, followed by extraction into dichloromethane and recrystallization from acetonitrile. The composition and a high level of purity for ^{4}**Q1**, were established by FTIR (type; ν/cm^{-1}): [P–O 1061, 1031; W–O (terminal) 950; W–O–W (corner-sharing WO_6 octahedra) 880; W–O–W (edge-sharing octahedra) 806], magnetic susceptibility ($\mu_{eff} = 8.9\mu_B$ mol^{-1} at 298 K), ^{31}P NMR (one very broad signal), UV-VIS ($\lambda_{max} = 262$ nm, $\varepsilon = 4.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}), EPR and potentiometric titration.

Table 1 Oxidation of alkenes by H_2O_2 catalysed by representative polyoxometalates[a]

POM[b]	$[H_2O_2]_0$/ $[H_2O_2]_f$ /mol dm^{-3}	Time /h	Substrate	Products (Yield,%)[c]	S^d (%)	T^e
$^4Q_{10}[Fe_4(B\text{–}PW_9O_{34})]_2$	0.2/0.02	3	cyclohexene	oxide (31) enol (0.8) enone (2.0)	95	15
$4Q_5[(Fe^{II})PW_{11}O_{39}]$	0.2/0.16	27	cyclohexene	oxide (3.7) enone (45)	15	2.5
$4Q_4Na_3[PW_{11}O_{39}]$	0.2/0.0	23	cyclohexene	oxide (90)	100	46
$^4Q_3\{PO_4[W(O)(O_2)_2]_4\}$	0.2/0.0	24	cyclohexene	oxide (82) enol (0.4) enol (0.4)	99	41
none	1.0/0.36	16	cyclohexene	(<0.1)		
$^4Q_{10}[Fe_4(B\text{–}PW_9O_{34})]_2$	0.2/0.01	25	1-octene	oxide (13)	80	6.2
$^4Q_4Na_3[PW_{11}O_{39}]$	0.2/0.0	23	1-octene	oxide (70)	90	20

[a] Reaction conditions: 20 °C, [POM] = polyoxometalate = 4 mmol dm^{-3}, [alkene substrate] = 1 mol dm^{-3} in 1 cm^3 of acetonitrile. [b] $^4Q = n\text{-}Bu_4N^+$. [c] Yield on peroxide consumed (ΔH_2O_2). [d] Selectivity for oxide formation = mol of oxide/mol of all organic products. [e] Turnover number = mol of all products/mol catalyst.

Table 1 summarizes the reaction conditions and the product distributions for epoxidation of two representative alkenes, cyclohexene and the terminal alkene, 1-octene, by H_2O_2 catalysed by four catalysts under single-phase homogeneous conditions in acetonitrile, a more desirable reaction medium than one containing chlorocarbons. The catalysts are the ^{4}Q salts of **1**, a conventional d-electron transition metal-substituted polyoxometalate (TMSP) complex of the Keggin class, $[(Fe^{II})PW_{11}O_{39}]^{5-}$, the Venturello complex, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, and one of the Ishii precursors to this complex, the Keggin lacunary complex, $[PW_{11}O_{39}]^{7-}$. In a typical reaction, 1.0 mmol of alkene was added to a solution of 0.004 mmol of the catalyst in 1.0 cm^3 of acetonitrile. To this was added 25 mm^3 of 30% aqueous H_2O_2. The resulting homogeneous reaction was stirred at 20 °C for the reaction times given in Table 1 then the products were identified and quantified by gas chromatography, GC/MS, and iodometric analysis. Although all the manipulations and the reactions in Table 1 were conducted under Ar, a control reaction indicated that deliberate addition of air had no marked effect on the observed distributions of organic products in the epoxidations catalysed by **1**. Whereas the reactions catalysed by $[(Fe^{II})PW_{11}O_{39}]^{5-}$ are of very low selectivity for epoxide (the kinetic selectivity is for the allylic oxidation products), the reactions catalysed by **1**, like those catalysed by $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ or its precursor complexes, are highly selective for epoxide. The modest yields based on H_2O_2 for the reactions catalysed by **1** result from the competing disproportionation of the H_2O_2 to O_2 and H_2O. The electronic absorption and ^{31}P NMR spectra of **1** before and after reaction were the same.

Table 2 summarizes representative product distributions in alkene epoxidation by H_2O_2 catalysed by **1** under conditions similar to those used in Table 1. The selectivity for epoxide is high in all cases, except for the stilbenes, where oxidative cleavage is substantial. Unlike the Venturello/Ishii systems, a small amount of unactivated C–H bond cleavage is noted in the **1**/H_2O_2 system. This point and the loss of stereoselectivity in *cis*-stilbene epoxidation are consistent with a higher degree of radical character in the substrate attack process of the mechanism and/or a higher steady state concentration of

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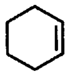
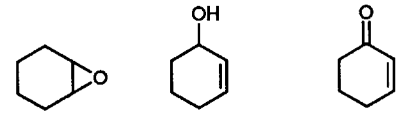
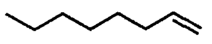
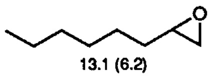
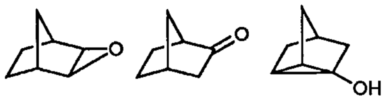
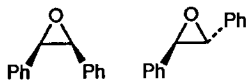
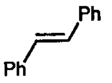
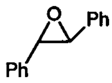
Table 2 Organic products from oxidation of representative alkenes by H_2O_2 catalysed by $^4Q_{10}[(Fe^{II})_4(B-PW_9O_{34})_2]$, ^{4}Q1[a]

Substrate	Products Yield on ΔH_2O_2(turnovers of ^{4}Q1)[b]
	 30.7 (13.7) 0.8 (0.4) 2.0 (0.9)
	 13.1 (6.2)
	 19.1 (8.6) 0.8 (0.4) 0.7 (0.3)
	 8.4 (4.0) 4.6 (2.2) PhCHO 14.5 (3.4)
	 2.0 (0.9) PhCHO 22.4 (5.1)

[a] $^4Q = n\text{-}Bu_4N^+$; Reaction conditions: 20 °C, $[^4Q1] = 4$ mmol dm^{-3}, [alkene substrate] = 1 mol dm^{-3}, $[H_2O_2] = 0.2$ mol dm^{-3} in 1 mm^3 of acetonitrile. [b] Yield of product based on H_2O_2 consumed = mol product/mol ΔH_2O_2.

freely diffusing radical intermediates in the **1**/H_2O_2 *versus* the Venturello/Ishii systems.

Initial rate constants for generation of 1,2-epoxyoctane by H_2O_2 oxidation of oct-l-ene catalysed by **1**, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ and $[PW_{11}O_{39}]^{7-}$ are similar ($k = 0.6$, 1.2 and 0.8×10^{-6} dm^3 mol^{-1} s^{-1}, respectively). In contrast to the instability of the parent Keggin complex, $[PW_{12}O_{40}]^{3-}$ and the lacunary complex, $[PW_{11}O_{39}]^{7-}$, with respect to degradation in the presence of aqueous H_2O_2, **1** proved to be quite stable. In a high turnover reaction, **1** catalysed the production of 1927 equivalents of cyclohexene oxide per equivalent of **1** when 8000 equivalents of H_2O_2 were added in four equal portions over a four-day period.

Several points of mechanistic or practical significance follow from the above data. First, the use of Q (*versus* Ishii's cetylpyridinium) as the solubilizing cation facilitates the homogeneous one-phase epoxidation by H_2O_2 catalysed by polyoxotungstate complexes in aqueous acetonitrile. The latter medium is preferable to the less tractable and more toxic two-phase conditions used in the Venturello and Ishii systems. Furthermore, the epoxidation of alkenes by H_2O_2 catalysed by $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ and $[PW_{11}O_{39}]^{7-}$ works at least as well in homogeneous aqueous acetonitrile using the Q salts of the catalysts (Table 1) as it does in water/chlorocarbons. Second, the solvolytic stability of **1** with respect to 30% aqueous peroxide is orders of magnitude higher than that of the Ishii precursor complexes $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$, and third, a related point, catalysis by **1** persists longer than that seen in the Venturello/Ishii chemistry after formation of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$. Fourth, the combination of the early reaction time kinetics and the spectroscopic data indicate that unlike the Ishii chemistry, generation of the Venturello active oxidant, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, from **1** is not facile, nor does $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ play a major role in the activation or transfer of oxygen from H_2O_2. The species responsible for attack on substrate could well be a high-valent radicaloid iron-oxo group, a thoroughly documented intermediate in a host of catalytic organic oxygenation processes,[11] or, less likely, an electrophilically-activated and transition metal-bound peroxide species analogous to the oxidizing intermediates in the well known olefin oxygenation processes that proceed by heterolytic mechanisms, including the commercially significant Halcon process and the Sharpless chiral epoxidation technology.[1,12,13]

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