Homogeneous Catalysis

A Highly Active Protonated Tetranuclear Peroxotungstate for Oxidation with Hydrogen Peroxide**

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Selective oxygen transfer to organic substrates with H₂O₂ as a terminal oxidant is important in industrial and synthetic chemistry because of the high content of active oxygen species in H₂O₂ and coproduction of only water. Therefore, a large number of complexes of titanium, vanadium, iron, manganese, tungsten, rhenium, and platinum have been developed for catalytic oxidation of various kinds of organic substrates with H_2O_2 .^[1-4] Among these systems, selective oxidation by tungsten-based catalysts with H₂O₂ has been widely investigated because of their high reactivity for oxidation as well as an inherent poor activity for the decomposition of H₂O₂. While peroxotungstates,^[5-8] transition-metal-substituted polyoxotungstates,^[9] and lacunary polyoxotungstates^[10] efficiently catalyze H₂O₂-based selective oxidation of alkenes, alcohols, amines, sulfides, and silanes, these systems have some drawbacks: 1) use of an excess of H_2O_2 with respect to the substrates, 2) low turnover numbers (TONs), 3) limited substrate scope, and/or 4) requirement of microwave irradiation or additives. Therefore, developments of efficient tungsten-based catalysts for green oxidation with H₂O₂ applicable to a wide range of substrates are still in great demand.

Various d⁰-transition-metal peroxo complexes with η^2 -O₂,^[5,6,11] μ - η^1 : η^2 -O₂,^[7] and μ - η^1 : η^1 -O₂^[8] groups have been proposed as active species for the epoxidation of alkenes with H₂O₂. For titanium and molybdenum complexes, spectroscopic and computational studies show that alkyl hydroperoxides, H₂O₂, and protons play an important role in formation of active species such as metal-bound alkylperoxides and hydroperoxides.^[12,13] While it has also been reported that epoxidation rates for tungsten complexes increase as the acidity of the reaction media increases,^[14] the reaction mechanism, including the role of the acidity, is still

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unclear. During the course of our investigation into the effects of protons on the epoxidation of alkenes catalyzed by a dinuclear peroxotungstate $[{WO(O_2)_2}_2(\mu-O)]^{2-}$, we successfully synthesized a novel protonated tetranuclear peroxotungstate TPA₃[H{W₂O₂(O₂)₄(μ -O)}₂] (**1**, TPA = $[(nC_3H_7)_4N]^+$). Herein, we report the **1**-catalyzed selective oxidation of various kinds of alkenes, sulfides, amines, and a silane under almost stoichiometric conditions (1.0– 1.5 equivalents). Compound **1** shows the highest catalytic activity reported to date for epoxidation of cyclooctene with H₂O₂ among various peroxotungstates including di- and tetranuclear peroxotungstates with XO₄^{*n*-} ligands (X = Se, S, As, P, and Si).

The effects of protons on epoxidation of cyclooctene catalyzed by $TPA_2[\{WO(O_2)_2\}_2(\mu-O)]$ were investigated (Figure 1). While epoxidation barely occurred in the absence



Figure 1. Dependences of the reaction rates on the amounts of HClO₄ added. Reaction conditions: TPA₂[{WO(O₂)₂}₂(μ -O)] (0.71 mM), cyclooctene (0.14 M), H₂O₂ (0.14 M), H₂O (0.56 M), HClO₄ (0–0.71 mM), acetonitrile (7 mL), 305 K.

of HClO₄, the catalytic activity of TPA₂[{WO(O₂)₂]₂(μ -O)] was dramatically enhanced by around 60 times after the addition of HClO₄. The reaction rates linearly increased as the amounts of HClO₄ increased, and did not change much upon addition of 0.5 equivalents or more of HClO₄. Epoxidation also efficiently proceeded with HNO₃ instead of HClO₄. Such a remarkable acceleration by addition of an acid has not been reported to date for dinuclear peroxotungstate-catalyzed epoxidation with H₂O₂. The ¹⁸³W NMR spectrum of TPA₂[{WO(O₂)₂]₂(μ -O)] showed one signal at -589 ppm ($\Delta \nu_{1/2}$ =42.1 Hz). Upon addition of 0.5 equivalents of HClO₄, a new signal appeared at -566 ppm ($\Delta \nu_{1/2}$ =1.2 Hz), and the signal at -589 ppm disappeared. These results show that

 $TPA_2[\{WO(O_2)_2\}_2(\mu-O)]$ reacts with 0.5 equivalents of an acid to form a new peroxotungstate, which would catalyze the epoxidation.

A TPA salt of a novel tetranuclear peroxotungstate (1) was synthesized by the reaction of $\text{TPA}_2[\{WO(O_2)_2\}_2(\mu-O)]$ with HNO₃. Single crystals of 1 suitable for X-ray structure analysis were successfully obtained from the reaction solution by vapor diffusion of diethyl ether.^[15] The molecular structure of the anionic part of 1 is shown in Figure 2. This part consists



Figure 2. Molecular structure of the anionic part of 1. Therman elliposoids set at 50% probability.

of two $[{WO(O_2)_2}_2(\mu-O)]^{2-}$ units that form the tetranuclear tungsten-oxygen cluster. The tungsten atoms have two differently bound peroxo ligands, namely η^2 -O₂ and μ - η^1 : η^2 -O₂. The O-O (1.49-1.54 Å), W-O(peroxo) (1.90-2.04 Å), W-OW (1.95-2.03 Å), and W=O (1.69-1.76 Å) bond lengths are typical for peroxotungstates.^[5–9] The existence of three TPA cations per anion implies that the anion charge is -3. The bond valence sum (BVS) values of tungsten (6.26-6.50) atoms in **1** indicate the valence of +6. The distance between O21 and O22 was 2.43 Å, thus suggesting the formation of a hydrogen-bonding network.^[16] The BVS values of O21 and O22 were 1.75 and 1.54, respectively. These results show that one proton is disordered over O21 and O22.^[17] The IR and Raman bands in the ranges 980-960, 860-840, and 580-510 cm⁻¹ are assignable to v(W=O), v(O-O), and v(W(O₂)), respectively, and these band positions are close to those of peroxotungstates.^[5-9] The X-ray, elemental analysis, IR, and Raman data show that the formula of 1 is TPA₃[H- $\{W_2O_2(O_2)_4(\mu-O)\}_2$. It has been reported that ¹H NMR signals of protons with strong intramolecular O-H-O hydrogen bonds (d(O-O) = 2.41 - 2.55 Å) appear in the range 19.0-14.9 ppm.^[16,18] Therefore, the signal at 15.8 ppm is assignable to the proton of the intramolecular O-H-O hydrogen bond (Figure S2(a) in the Supporting Information). The ¹⁸³W NMR spectrum of **1** in CD₃CN showed one signal at -566 ppm $(\Delta v_{1/2} = 1.6 \text{ Hz}; \text{Figure S2(b)})$, thus suggesting that **1** is a single species. These results show that the solid-state structure of the anionic part of 1 is maintained in solution. Stoichiometric oxidation of triphenylphosphine (1 mmol) with **1** (10 µmol) gave 81 µmol of triphenylphosphine oxide, thus showing that **1** has 8 equivalents of active oxygen species.^[19] On the other hand, stoichiometric epoxidation of cyclooctene (1 mmol) with **1** (20 µmol) at 293 K for 12 h produced 58 µmol of the corresponding epoxide. All peroxo groups did thus not react with cyclooctene, in contrast with triphenylphosphine, and such stoichiometry has also been observed for stoichiometric epoxidation of (*R*)-(+)-limonene with the di- and tetranuclear peroxotungstates with XO₄^{*n*-} ligands (X = S, As, P, etc.).^[7]

Epoxidation of cyclooctene with H_2O_2 was carried out under various conditions (Table S5). The **1**-catalyzed epoxidation efficiently proceeded to give 1,2-epoxycyclooctane in 86% yield with only one equivalent of H_2O_2 with respect to cyclooctene. The reaction rate $((1.31\pm0.10)~\text{mM\,min^{-1}})$ of **1** was almost the same as that $((1.42\pm0.18)~\text{mM\,min^{-1}})$ of a mixture of TPA₂[{WO(O_2)_2]_2(\mu-O)] and 0.5 equivalents of HClO_4.^[20] Other oxidants were not effective for the present epoxidation. Among the solvents tested, acetonitrile was the most effective.

The catalytic activity of 1 was compared with those of diand tetranuclear peroxotungstates with XO_4^{n-} ligands (X = Se, S, As, P, and Si) for epoxidation of cyclooctene with H_2O_2 (Figure S4). The turnover frequency (TOF (determined by the initial rate), $314 h^{-1}$) of **1** was much larger than those $(<0.1-63 h^{-1})$ of the other peroxotungstates. In order to investigate the high catalytic activity of 1, the structural data were compared. It has been reported that the reaction rates for di- and tetranuclear peroxotungstates increase as the W-O bond lengths in peroxotungstates with the XO_4^{n-} ligands (XO-W) increases, and that epoxidation efficiently proceeds using peroxotungstates with weakly coordinated XO4ligands (i.e., longer XO-W bond lengths).^[7d] Such a pushpull ligand effect modifies the Lewis acidity of tungsten atoms and the activity of peroxo ligands. The W-O bond lengths of 1 (W2–O22 = 2.03 Å) were longer than those (1.94–2.01 Å) of the other peroxotungstates (Figure S5), in agreement with the highest catalytic activity of **1**. Thus, the proton in **1** plays an important role in increasing the Lewis acidity of the tungsten atoms.

The scope of this catalytic system for oxidation of various kinds of alkenes, sulfides, amines, and a silane was investigated (Table 1). Cyclic and internal alkenes could selectively be transformed to the corresponding epoxides in high yields by using an almost-stoichiometric amount of H₂O₂ (1.0-1.5 equivalents; Table 1, entries 1-7). For epoxidation of cisand trans-2-octenes, the configurations around the C=C moieties were retained in the corresponding epoxides, thus suggesting that free-radical intermediates are not involved in this reaction. Epoxidation of dicyclopentadiene gave the corresponding diepoxide in 93% yield (Table 1, entry 8). 1-Octene was also efficiently oxidized to the corresponding epoxide (Table 1, entry 9). Thioanisole and methyl n-octyl sulfide could selectively be transformed to the corresponding sulfoxides in high yields (Table 1, entries 10 and 11). Di-nbutylamine and aniline were oxidized to the corresponding nitrone and nitroso compounds in 84 and 85% yields, respectively (Table 1, entries 12 and 13). Triethylsilane was



Table 1: Selective oxidation of various substrates with H_2O_2 catalyzed by $1^{[a]}$

Entry	Substrate	<i>t</i> [h]	Product	Yield [%] (selectivity [%])
1	\bigcirc	10	\bigcirc	81 (94)
2 ^[b,c]	\bigcirc	8	\bigcirc	77 (88)
3	\bigcirc	10	$\bigcirc \circ$	92 (>99)
4 ^[c,d]		9	o	94 (>99)
5 ^[b]	nC ₅ H ₁₁	5	nC ₅ H ₁₁	71 (95)
6 ^[c,e]	nC5H11	13	nC ₅ H ₁₁	77 (92)
7 ^[b]	À	9	20	74 (89)
8 ^[b,c,f]		7	o C	93 (93)
9 ^[e,g]	nC ₆ H ₁₃	10	nC ₆ H ₁₃	72 (95)
10 ^[h]	S_	3	Š,	80 (91)
11 ^[h]	_S_nC ₈ H ₁₇	2		83 (94)
12 ^[d,i]	nC ₃ H ₇ NH nC ₄ H ₉	11	nC ₃ H ₇	84 (85)
13 ^[d,i]		2	N=O	85 (86)
14 ^[d]	Et ₃ SiH	3	Et ₃ SiOH	76 (87)

[a] Reaction conditions: 1 (2.5 μ mol), substrate (1 mmol), 30% H₂O₂ (1 mmol), acetonitrile (6 mL), under air (1 atm), reaction temperature 273 K (entries 10 and 11), 293 K (entries 1, 2, 6, 7, and 9), 305 K (entry 3), 313 K (entries 4, 5, 8, 12, and 14), and 323 K (entry 13). Yield (%) = amount of product [mol]/amount of substrate [mol] × 100. [b] 1 (10 μ mol). [c] 30% H₂O₂ (1.5 mmol). [d] 1 (5 μ mol). [e] 1 (20 μ mol). [f] Substrate (0.5 mmol). [g] Substrate (5 mmol). Yield (%) = amount of H₂O₂ [mol] × 100. [h] 1 (0.6 μ mol). [i] 30% H₂O₂ (2 mmol).

selectively converted to triethylsilanol (Table 1, entry 14). To the best of our knowledge, a simple peroxotungstate that does not have ligands and/or additives and is highly efficient for H_2O_2 -based oxidation of a wide range of substrates has not been reported to date.

In order to further confirm the effectiveness of the present system, a 20 mmol scale epoxidation of cyclooctene was carried out. The epoxidation proceeded efficiently, and the corresponding epoxide could be isolated in 86% yield [Eq. (1)]. The TOF (determined by the initial rate) was $1500 h^{-1}$ and the TON reached up to 1720. The TON was much larger than those of the tungsten-based catalysts such as $WO_2Cl_2(OPPh_2CH_2OH)_2$ (82),^[5a] [bmim]₃[PW₁₂O₄₀] (290; bmim = 1-butyl-3-methylimidazolium),^[21] Na₂WO₄/NH₂-



 $\begin{array}{lll} CH_2PO_3H_2/TOMAHSO_4 & (490; & TOMA = [(nC_8H_{17})_3-(CH_3)N]^+), ^{[14a]} & THA_2[\{WO(O_2)_2\}_2(\mu-O)] & (600; & THA = [(nC_6H_{13})_4N]^+), ^{[7c]} & PW_{12}O_{40}/Im-SiO_2 & (648; & Im-SiO_2 = imida-zole functionalized silica), ^{[22]} and W-Zn/SnO_2 & (650)^{[23]} & under almost-stoichiometric conditions (substrate:H_2O_2 = 1:1.0-1.5; Table S6). ^{[24]} \end{array}$

Kinetic studies on the epoxidation of cyclooctene with H_2O_2 catalyzed by **1** showed the first-order dependence of the reaction rates on concentration of **1** (0.23–1.44 mM) and cyclooctene (0.04–0.43 M; Figure S6). The reaction rate was not dependent on the concentration of H_2O_2 (0.04–0.43 M), and the dependence was different from that of $[\{WO(O_2)_2\}_2(\mu-O)]^{2^-}$: The $[\{WO(O_2)_2\}_2(\mu-O)]^{2^-}$ -catalyzed epoxidation shows a first-order dependence of the reaction rate on the concentration of H_2O_2 .^[8] In addition, the catalytic epoxidation rate of **1** was sixty times larger than that of $[\{WO(O_2)_2\}_2(\mu-O)]^{2^-}$. All these results suggest that **1** is the catalytically active species and that the reaction of an alkene with **1** is the rate-determining step.

In conclusion, catalytic epoxidation by a dinuclear peroxotungstate $[{WO(O_2)_2}_2(\mu-O)]^{2-}$ was dramatically accelerated by the addition of 0.5 equivalents of an acid, and a novel tetranuclear peroxotungstate **1** was successfully synthesized by the reaction of $[{WO(O_2)_2}_2(\mu-O)]^{2-}$ with an acid. Compound **1** showed high catalytic activity for selective oxidation of various kinds of alkenes, sulfides, amines, and a silane with 1.0–1.5 equivalents of H₂O₂.

Experimental Section

Synthesis and characterization of 1: TPA₂[{WO(O₂)₂]₂(μ -O)] (see the Supporting Information; 53 mg, 58 µmol) and 70 % HNO₃ (100 µmol) were dissolved in a solution of 30 % aqueous H₂O₂ (0.05 mL) in acetonitrile (0.5 mL). Diethyl ether (0.5 mL) was added to the resulting solution. Colorless crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of diethyl ether into the solution at 277 K. Yield: 33 mg (69 %). ¹⁸³W NMR (11.20 MHz, CD₃CN, 253 K, Na₂WO₄): δ = -565.6 (Δ v_{1/2} = 1.6 Hz). IR (KCI): $\tilde{\nu}$ = 1038, 981, 967, 844, 755, 707, 670, 642, 585, 573, 511, 377 cm⁻¹. Raman: $\tilde{\nu}$ = 1136, 1105, 1036, 973, 859, 580, 526, 309 cm⁻¹. Elemental analysis calcd (%) for C₃₆H₈₅N₃O₂₂W₄ (TPA₃[H{W₂O₂(O₂)₄(μ -O)}₂]): C 26.25, H 5.20, N 2.55, W 44.64; found: C 26.01, H 5.31, N 2.53, W 44.45.

Typical procedure for catalytic oxidation with H_2O_2 : The solvent, substrate, and oxidant were introduced into a glass tube (30 mL) containing a magnetic stirrer bar. The reaction was initiated by addition of the catalyst, and the reaction solution was periodically analyzed by GC. Before the GC analysis for the oxidation of sulfides, the remaining H_2O_2 was decomposed at 273 K by addition of Ru(OH)_x/Al₂O₃.^[26] All products were known compounds and identified by comparison of their retention times, mass spectra, and NMR spectra with those of authentic samples.

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