Homogeneous Catalysis

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

*Ryo Ishimoto, Keigo Kamata, and Noritaka Mizuno**

Selective oxygen transfer to organic substrates with H_2O_2 as a terminal oxidant is important in industrial and synthetic chemistry because of the high content of active oxygen species in H_2O_2 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 H_2O_2 has been widely investigated because of their high reactivity for oxidation as well as an inherent poor activity for the decomposition of H_2O_2. While peroxotungstates,[5–8] transition-metal-substituted polyoxotungstates,[9] and lacunary polyoxotungstates[10] efficiently catalyze H_2O_2-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 H_2O_2 applicable to a wide range of substrates are still in great demand.

Various d^0-transition-metal peroxo complexes with η^2-O_2,[5,6,11] μ-η^1:η^2-O_2,[7] and μ-η^1:η^1-O_2[8] groups have been proposed as active species for the epoxidation of alkenes with H_2O_2. For titanium and molybdenum complexes, spectroscopic and computational studies show that alkyl hydroperoxides, H_2O_2, 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 unclear. During the course of our investigation into the effects of protons on the epoxidation of alkenes catalyzed by a dinuclear peroxotungstate $[\{WO(O_2)_2\}_2(\mu\text{-}O)]^{2-}$, we successfully synthesized a novel protonated tetranuclear peroxotungstate $TPA_3[H\{W_2O_2(O_2)_4(\mu\text{-}O)\}_2]$ (**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 H_2O_2 among various peroxotungstates including di- and tetranuclear peroxotungstates with XO_4^{n-} ligands (X = Se, S, As, P, and Si).

The effects of protons on epoxidation of cyclooctene catalyzed by $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ were investigated (Figure 1). While epoxidation barely occurred in the absence of $HClO_4$, the catalytic activity of $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ was dramatically enhanced by around 60 times after the addition of $HClO_4$. The reaction rates linearly increased as the amounts of $HClO_4$ increased, and did not change much upon addition of 0.5 equivalents or more of $HClO_4$. Epoxidation also efficiently proceeded with HNO_3 instead of $HClO_4$. Such a remarkable acceleration by addition of an acid has not been reported to date for dinuclear peroxotungstate-catalyzed epoxidation with H_2O_2. The ^{183}W NMR spectrum of $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ showed one signal at -589 ppm ($\Delta\nu_{1/2}$=42.1 Hz). Upon addition of 0.5 equivalents of $HClO_4$, 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

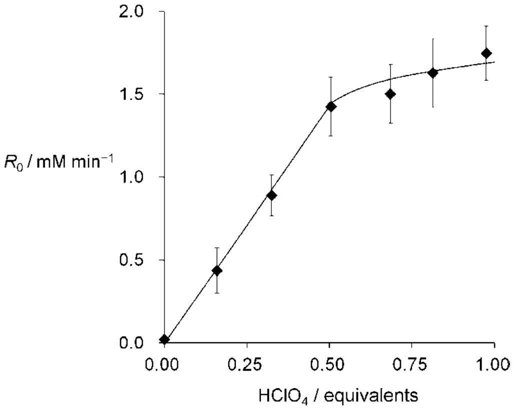

Figure 1. Dependences of the reaction rates on the amounts of $HClO_4$ added. Reaction conditions: $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$ (0.71 mM), cyclooctene (0.14 M), H_2O_2 (0.14 M), H_2O (0.56 M), $HClO_4$ (0–0.71 mM), acetonitrile (7 mL), 305 K.

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[*] R. Ishimoto, Dr. K. Kamata, Prof. Dr. N. Mizuno
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp
Homepage: http://park.itc.u-tokyo.ac.jp/mizuno/

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$TPA_2[\{WO(O_2)_2\}_2(\mu\text{-O})]$ 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 $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-O})]$ with HNO_3. 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 of two $[\{WO(O_2)_2\}_2(\mu\text{-O})]^{2-}$ units that form the tetranuclear tungsten–oxygen cluster. The tungsten atoms have two differently bound peroxo ligands, namely η^2-O_2 and μ-η^1:η^2-O_2. 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 ν(W=O), ν(O−O), and ν(W(O$_2$)), 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 $TPA_3[H\{W_2O_2(O_2)_4(\mu\text{-O})\}_2]$. It has been reported that ^{1}H 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 ^{183}W NMR spectrum of **1** in CD_3CN showed one signal at −566 ppm ($\Delta\nu_{1/2}$=1.6 Hz; 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 XO_4^{n-} ligands (X = S, As, P, etc.).[7]

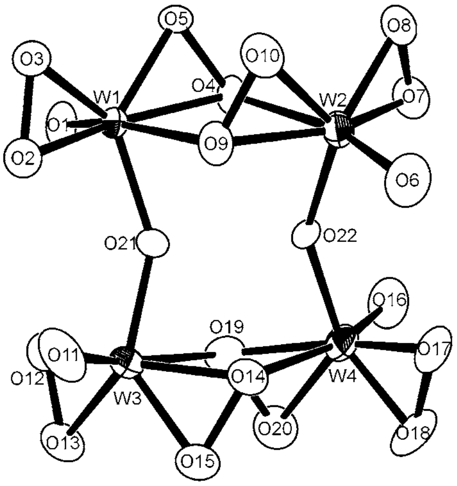


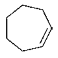
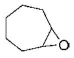
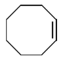
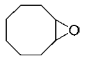
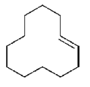
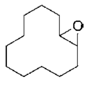
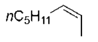
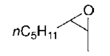
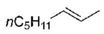
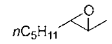
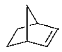
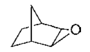
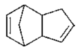
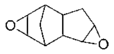
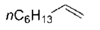
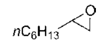
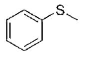
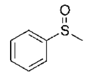
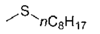
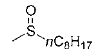
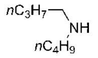
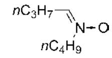
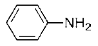
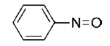
Figure 2. Molecular structure of the anionic part of **1**. Therman elliposoids set at 50% probability.

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 ± 0.10) mM min^{-1}) of **1** was almost the same as that ((1.42 ± 0.18) mM min^{-1}) of a mixture of $TPA_2[\{WO(O_2)_2\}_2(\mu\text{-O})]$ 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 di- and 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 XO_4^{n-} ligands (i.e., longer XO−W bond lengths).[7d] Such a push–pull 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 H_2O_2 (1.0–1.5 equivalents; Table 1, entries 1–7). For epoxidation of *cis*- and *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-*n*-butylamine 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

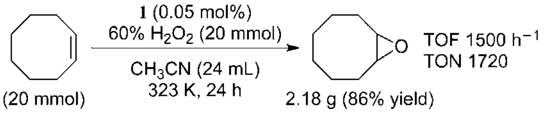
Table 1: Selective oxidation of various substrates with H_2O_2 catalyzed by **1**.[a]

Entry	Substrate	t [h]	Product	Yield [%] (selectivity [%])
1		10		81 (94)
2[b,c]		8		77 (88)
3		10		92 (>99)
4[c,d]		9		94 (>99)
5[b]		5		71 (95)
6[c,e]		13		77 (92)
7[b]		9		74 (89)
8[b,c,f]		7		93 (93)
9[e,g]		10		72 (95)
10[h]		3		80 (91)
11[h]		2		83 (94)
12[d,i]		11		84 (85)
13[d,i]		2		85 (86)
14[d]	Et_3SiH	3	Et_3SiOH	76 (87)

[a] Reaction conditions: **1** (2.5 μmol), substrate (1 mmol), 30% H_2O_2 (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 μmol). [c] 30% H_2O_2 (1.5 mmol). [d] **1** (5 μmol). [e] **1** (20 μmol). [f] Substrate (0.5 mmol). [g] Substrate (5 mmol). Yield (%) = amount of product[mol]/initial amount of H_2O_2[mol] × 100. [h] **1** (0.6 μmol). [i] 30% H_2O_2 (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]$_3$[$PW_{12}O_{40}$] (290; bmim = 1-butyl-3-methylimidazolium),[21] $Na_2WO_4/NH_2CH_2PO_3H_2$/TOMAHSO$_4$ (490; TOMA = [$(nC_8H_{17})_3(CH_3)N$]$^+$),[14a] THA$_2$[$\{WO(O_2)_2\}_2(\mu\text{-}O)$] (600; THA = [$(nC_6H_{13})_4N$]$^+$),[7c] $PW_{12}O_{40}$/Im-SiO$_2$ (648; Im-SiO$_2$ = imidazole 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]



(1)

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 [$\{WO(O_2)_2\}_2(\mu\text{-}O)$]$^{2-}$: The [$\{WO(O_2)_2\}_2(\mu\text{-}O)$]$^{2-}$-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 [$\{WO(O_2)_2\}_2(\mu\text{-}O)$]$^{2-}$. 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 [$\{WO(O_2)_2\}_2(\mu\text{-}O)$]$^{2-}$ 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 [$\{WO(O_2)_2\}_2(\mu\text{-}O)$]$^{2-}$ 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 H_2O_2.

Experimental Section

Synthesis and characterization of **1**: TPA$_2$[$\{WO(O_2)_2\}_2(\mu\text{-}O)$] (see the Supporting Information; 53 mg, 58 μmol) and 70% HNO_3 (100 μmol) were dissolved in a solution of 30% aqueous H_2O_2 (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%). ^{183}W NMR (11.20 MHz, CD_3CN, 253 K, Na_2WO_4): $\delta = -565.6$ ($\Delta\nu_{1/2} = 1.6$ Hz). IR (KCl): $\tilde{\nu} =$ 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 $C_{36}H_{85}N_3O_{22}W_4$ (TPA$_3$[$H\{W_2O_2(O_2)_4(\mu\text{-}O)\}_2$]): 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 $Ru(OH)_x/Al_2O_3$.[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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Keywords: epoxidation · homogeneous catalysis · hydrogen peroxide · Lewis acids · peroxotungstates

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[15] CCDC 865334 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic and structural data are summarized in Tables S1 and S2 in the Supporting Information, respectively.

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