A novel Ti–O–Ti bonding species constructed in a metal-oxide cluster [{Ti(OH$_2$)(ox)}$_2$(μ-O)(α-PW$_{11}$O$_{39}$)]$^{5-}$ as a precatalyst: Epoxidation of alkenes with hydrogen peroxide[☆]

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Abstract

A novel Ti–O–Ti bonding complex constructed in the monomeric, mono-lacunary α-Keggin polyoxotungstate, [{Ti(OH$_2$)(ox)}$_2$(μ-O)(α-PW$_{11}$O$_{39}$)]$^{5-}$ (1) can act as a precatalyst for the epoxidation of cyclooctene, cyclohexene, and 1-octene with aqueous H$_2$O$_2$ at 25 °C in a homogeneous system. The catalytic activities of complex 1 were considerably higher than those of dimeric mono-, di-, and tri-titanium(IV)-substituted Keggin polyoxotungstates [(α-PTiW$_{11}$O$_{39}$)$_2$O]$^{8-}$ (2), [(α-1,2-PW$_{10}$Ti$_2$O$_{38}$)$_2$O$_2$]$^{10-}$ (3), and [(α-1,2,3-PTi$_3$W$_9$O$_{37}$)$_2$O$_3$]$^{12-}$ (4).
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Keywords: Titanium(IV); Polyoxotungstate; Alkene epoxidation; Hydrogen peroxide

1. Introduction

In academic and industrial fields, selective catalytic epoxidation of alkenes with an environmentally friendly oxidant, aqueous hydrogen peroxide (H$_2$O$_2$), is an interesting objective [1–5]. Transition metal-substituted polyoxometalates (POMs) have attracted considerable attention as oxidation catalysts because they are resistant to oxidative degradation. Further, the "active sites" of their transition metals and countercations can undergo extensive synthetic modifications [6–11].

Site-selective substitution of the W^{VI} atoms in POMs with Ti^{IV} atoms is of particular interest because of the multicentered active sites formed with corner-sharing and/or edge-sharing TiO$_6$ octahedra and the molecular modeling studies of various types of titanosilicates for oxidation catalysis [12–16]. Several H$_2$O$_2$-based oxidation reactions catalyzed by titanium(IV)-substituted POMs

have been described, e.g., monomeric, Keggin mono-titanium(IV)-substituted POM [α-PW$_{11}$TiO$_{40}$]$^{5-}$ [17–20] and its conjugated acid [α-P(TiOH)W$_{11}$O$_{39}$]$^{4-}$ [18,20]; dimeric, Keggin mono-titanium(IV)-substituted POM [(α-PTiW$_{11}$O$_{39}$)$_2$O]$^{8-}$ [20]; monomeric, Keggin 1,5-di-titanium(IV)-substituted POM [α-1,5-PW$_{10}$Ti$_2$O$_{40}$]$^{7-}$ [19,21,22]. Recently, we have reported the catalytic activities of dimeric mono-, di-, and tri-titanium(IV)-substituted Keggin polyoxotungstates [(α-PTiW$_{11}$O$_{39}$)$_2$O]$^{8-}$ (2), [(α-1,2-PW$_{10}$Ti$_2$O$_{38}$)$_2$O$_2$]$^{10-}$ (3), and [(α-1,2,3-PTi$_3$W$_9$O$_{37}$)$_2$O$_3$]$^{12-}$ (4) for epoxidation of alkenes with H$_2$O$_2$, in which the structure around the titanium centers had a strong influence on the catalytic activities [23].

In this paper, we focused on the novel Ti–O–Ti bonding complex constructed in the monomeric, mono-lacunary α-Keggin POM [24] [{Ti(OH$_2$)(ox)}$_2$(μ-O)(α-PW$_{11}$O$_{39}$)]$^{5-}$ (1) as a precatalyst for the epoxidation of various alkenes with H$_2$O$_2$ in a homogeneous system. The molecular structure of the potassium salt of complex 1 K$_5$[{Ti(OH$_2$)(ox)}$_2$(μ-O)(α-PW$_{11}$O$_{39}$)]·13H$_2$O (K-1) had an octahedral lacunary site (host) and two octahedral Ti groups (guest), i.e., it was the one host-two guests type POM, as shown in Fig. 1. Here, we also synthesized the organic solvent-soluble tetrabutylammonium (TBA) salt of complex 1 (Bu$_4$N)$_{4.5}$K$_{0.5}$[{Ti(OH$_2$)(ox)}$_2$(μ-O)(α-PW$_{11}$O$_{39}$)] (TBA-1) and compared the catalytic activities of TBA-1 with those of TBA salts of complexes
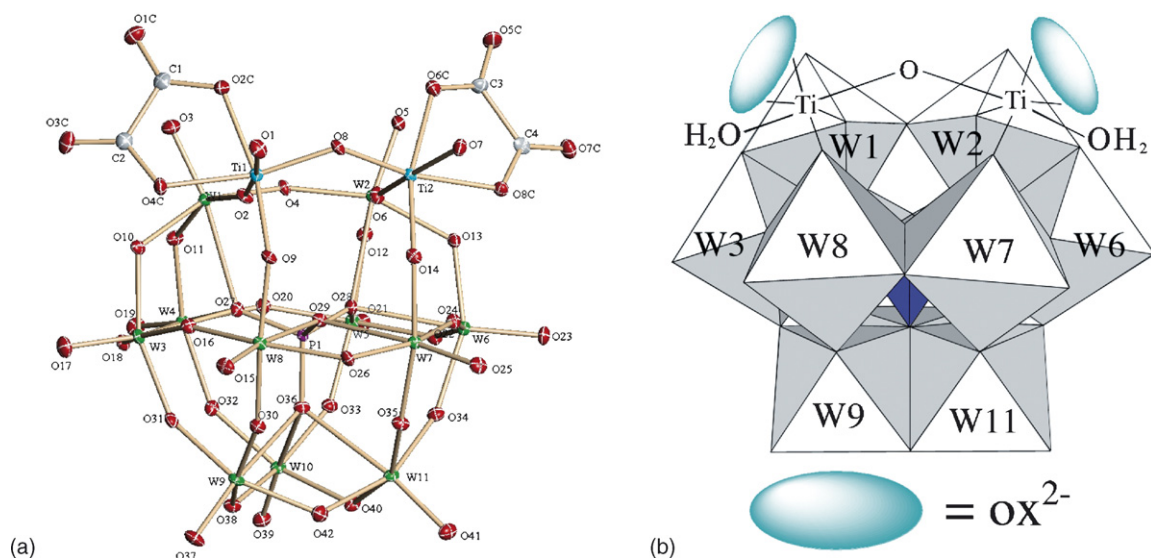
Fig. 1. (a) Molecular structure and (b) polyhedral representation of a novel Ti–O–Ti bonding complex constructed in the monomeric, mono-lacunary α-Keggin polyoxotungstate $[\{Ti(OH_2)(ox)\}_2(\mu\text{-}O)(\alpha\text{-}PW_{11}O_{39})]^{5-}$ (**1**). The WO_6 and internal PO_4 groups are represented by white/gray octahedra and deep blue tetrahedra, respectively.

2–4, $(Bu_4N)_7H[(PTiW_{11}O_{39})_2O]$ (TBA-2), $(Bu_4N)_7KH_2[(\alpha\text{-}1,2\text{-}PTi_2W_{10}O_{38})_2O_2]$ (TBA-3), and $(Bu_4N)_7KH_4[(\alpha\text{-}1,2,3\text{-}PTi_3W_9O_{37})_2O_3]$ (TBA-4) [23].

2. Experimental

2.1. Materials

The following chemicals were used as received: acetonitrile, 1,2-dichloromethane, cyclooctene, cyclohexene, 1-octene, 30% H_2O_2, and tetrabutylammonium bromide (TBABr) of quantitative analysis grade (all obtained from Wako); dimethylsulfoxide-d_6 and acetonitrile-d_3 (obtained from Isotec). K-1 was prepared in accordance with the literature [24].

2.2. Instrumentation and methods

$^{13}C\text{-}\{^1H\}$ (100.40 MHz) and $^{31}P\text{-}\{^1H\}$ NMR (161.70 MHz) spectra in solution were recorded in 5-mm outer diameter tubes on a JEOL JNM-EX 400 FT NMR spectrometer with a JEOL EX-400 NMR data-processing system. ^{13}C NMR spectra were measured in DMSO-d_6 solution with reference to an internal DSS. Chemical shifts are reported as positive for resonance downfield of DSS (δ 0). ^{31}P NMR spectra were measured in CD_3CN and DMSO-d_6 solutions referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts were reported on the δ scale with resonance upfield of H_3PO_4 (δ 0) as negative. The TG/DTA data were obtained using a Rigaku TG 8101D and TAS 300 data-processing system and the measurements were performed in air with a temperature ramp of 4 °C per min between 20 and 500 °C. Infrared spectra were recorded on a Jasco 300 FTIR spectrometer on KBr disks at room temperature. The elemental analyses were performed on a Perkin-Elmer 2400 CHNS Elemental Analyzer II at Kanagawa University and Mikroanalytisches Labor Pascher (Remagen, Germany).

2.3. Synthesis of $(Bu_4N)_{4.5}K_{0.5}[\{Ti(OH_2)(ox)\}_2(\mu\text{-}O)(\alpha\text{-}PW_{11}O_{39})]$ (TBA-1)

Tetrabutylammonium salt of $[\{Ti(OH_2)(ox)\}_2(\mu\text{–}O)(\alpha\text{-}PW_{11}O_{39})]^{5-}$ (**1**) was synthesized as follows: K-1 (0.5 g, 0.14 mmol) was dissolved in hot water (50 mL) at 90 °C for a few minutes, and then the clear colorless solution was cooled to 20 °C in a water bath. Excess Bu_4NBr (1.0 g, 3.0 mmol) was added to the clear colorless solution to form a pale-yellow precipitate. After stirring for 30 min in a water bath at 10 °C, the pale-yellow precipitate was collected on a membrane filter (J.G. type, 0.2 μm), and washed with water (10 mL × 1), ethanol (20 mL × 1) and then with ether (50 mL × 2). The crude precipitate was purified by reprecipitation from the DMSO/ethylacetate system at 25 °C, washed with ethylacetate (50 mL × 3) and then with ether (50 mL × 3); subsequently, it was dried in vacuo for 2 h. Yield: 0.32 g (55.0%). Elemental analysis: Found (calcd) for $(Bu_4N)_{4.5}K_{0.5}[\{Ti(OH_2)(ox)\}_2(\mu\text{-}O)(\alpha\text{-}PW_{11}O_{39})]$: C, 21.84% (22.20%); H, 3.94% (4.07%); N, 1.52% (1.53%); K 0.24% (0.48%). Infrared spectrum (cm^{-1}, Fig. S1): 1713(m), 1686(m), 1484(m), 1381(m), 1103(m), 1068(m), 1054(m), 960(s), 888(m), 808(vs), 521(m). ^{31}P NMR (in DMSO-d_6, at 25 °C, Fig. S2): δ −12.0 (major product), −13.6 (minor product due to **2** ca. 0.07%) [Note: the anionic oxalato titanium(IV) species, $[TiO(ox)_2]^{2-}$ was gradually removed from complex **1** in aqueous, acetonitorile, and DMSO solutions at 25 °C to yield a dimeric, mono-titanium(IV)-substituted polyoxometalates, complex **2**. To prevent the formation of complex **2**, TBA-1 was synthesized at ∼10 °C; however, only a small amount of complex **2** (<0.07%) was contaminated at the stage of addition of TBABr]. ^{13}C NMR (in DMSO-d_6, at 25 °C, Fig. S3): δ 168.5 (ox). TG/DTA data: 30.62% weight loss with four exthothermic points at 289.2, 328.5, 369.6, and 379.4 °C and an endothermic point at 362.0 °C resulting from the decomposition of Bu_4N^+ ions (calculated value for 4.5Bu_4N^+ ions was

27.28%) and two oxalate ligands (calculated value for $2(C_2O_4)$ was 3.71%). No weight loss due to solvated or absorbed water was observed.

2.4. Catalytic epoxidation

Homogeneous epoxidation reactions of cyclooctene, cyclohexene, and 1-octene catalyzed by organic solvent-soluble TBA-1 were carried out in a round-bottom flask or a Schlenk tube by mixing 4.35–7.70 mmol of substrate, 9.72 mmol of 30% H_2O_2, and 0.02 mmol of POMs in 1:1 (v/v) acetonitrile/CH_2Cl_2 (30 mL) under air at 25 °C. The reaction solution was periodically sampled after 5, 60, 180, and 240 min and these solution samples were analyzed by gas chromatography (TCD) on a DB-FFAP capillary column (0.53 mm × 15 m) and gas chromatography (FID) on a DB-WAX capillary column (0.53 mm × 15 m). The oxidation products were also analyzed by EI-MS and CI-MS spectroscopy (Shimadzu, GCMS-QP2010).

2.5. Acid/base titration of K-1

The titration was carried out with n-butylamine according to Ref. [25]. K-1 (35.0 mg, 10 μmol) was suspended in acetonitrile (50 mL) at room temperature and the suspension was stirred for 3 h. The titration data were obtained with a pH Meter (Denver Instrument). Data points were obtained in mV. A solution of n-butylamine (1×10^{-4} mol/L) was syringed into the suspension in 0.5-equivalent intervals.

3. Results and discussion

3.1. Homogeneous epoxidation of alkenes catalyzed by TBA-1 with H_2O_2

TBA-1 was used as a homogeneous precatalyst for the epoxidation of alkenes with H_2O_2, as shown in Table 1. Since the potassium salt of complex **1** was insoluble in organic solvents, tetrabutylammonium salt of complex **1** was prepared as a precatalyst. ^{31}P NMR spectra of TBA-1 in CD_3CN at 25 °C showed that TBA-1 was gradually decomposed to form complex **2** with the removal of the $[TiO(ox)_2]^{2-}$ species [24]. The decomposition of TBA-1 to complex **2** was observed to be faster due to the addition of H_2O_2 (Fig. S4); however, no signal due to Venturello complex $\{PO_3[W(O)(O_2)_2]_4\}^{3-}$ was observed in the range of -10 to $+40$ ppm [26]. Some POMs, e.g., $[P_2W_{15}V_3O_{62}]^{9-}$ and $[SiW_9V_3O_{40}]^{7-}$, are also unstable in the presence of H_2O_2 [27,28]. To compare the catalytic activities of TBA-1 with those of TBA-2–TBA-4, the catalytic activity of TBA-1 was determined for the initial 4 h. Due to the addition of H_2O_2, the colors of all the complexes changed from colorless to orange because of the formation of peroxotitanium(IV) and/or hydroperoxotitanium(IV) intermediates [20].

The time course for the epoxidation of cyclooctene (the ratio of [cyclooctene]/[H_2O_2] was 0.8), catalyzed by TBA-1 at 25 °C, was monitored by gas chromatography. Cyclooctene oxide was the major product (selectivity >99% was obtained for TBA-1–TBA-4), and no induction period was observed for this reaction (≥5 min). Only small amounts

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Table 1

Epoxidation of alkenes with H_2O_2 catalyzed by Ti^{IV}-substituted Keggin polyoxotungstates at 25 °C[a]

Substrate (mmol)	Catalyst	TOF (s^{-1})[b]	Selectivity of epoxidation (%)	Conversion (%)[c]
Cyclooctene (7.70)	$[\{Ti(OH_2)(ox)\}_2(\mu\text{-}O)(\alpha\text{-}PW_{11}O_{39})]^{5-}$ (**1**)	1.8×10^{-1}	>99	14.0
		$2.6 \times 10^{-2\,d}$	>99	24.3
	$[(\alpha\text{-}PTiW_{11}O_{39})_2O]^{8-}$ (**2**)	3.7×10^{-4}	>99[e]	2.88×10^{-2}
		$4.7 \times 10^{-4\,d}$	>99[e]	4.39×10^{-1}
	$[(\alpha\text{-}PTi_2W_{10}O_{38})_2O_2]^{10-}$ (**3**)	1.2×10^{-3}	>99[e]	9.35×10^{-2}
		$1.3 \times 10^{-3\,d}$	>99[e]	1.22
	$[(\alpha\text{-}PTi_3W_9O_{37})_2O_3]^{12-}$ (**4**)	4.8×10^{-3}	>99[e]	3.74×10^{-1}
		$3.6 \times 10^{-3\,d}$	>99[e]	3.37
Cyclohexene (4.93)	**1**	$1.2 \times 10^{-2\,f}$	>90[g]	70.1
	2	$\_^{f}$	–	–
	3	$7.6 \times 10^{-6\,f}$	83[g]	4.44×10^{-2}
	4	$1.2 \times 10^{-4\,f}$	86[g]	7.01×10^{-1}
1-Octene (6.37)	**1**	$2.8 \times 10^{-3\,h}$	>99[i]	9.49
	2	$\_^{h}$	–	–
	3	$5.4 \times 10^{-6\,h}$	>99[i]	1.83×10^{-2}
	4	$3.1 \times 10^{-5\,h}$	>99[i]	1.05×10^{-1}

[a] Reaction conditions: catalyst 0.02 mmol, substrates 4.93–7.70 mmol, 30% H_2O_2 9.72 mmol, solvent, 1:1 (v/v) CH_2Cl_2/CH_3CN 30 mL, under air.

[b] TOF = turnover number (TON) s^{-1} after 5 min.

[c] Conversion = (mol of products)/(mol of substrate) × 100.

[d] After 1 h.

[e] Cyclooctene oxide was epoxidation product.

[f] After 4 h.

[g] Cyclohexene oxide and cyclohexanediol were epoxidation products.

[h] After 3 h.

[i] 1,2-Epoxyoctane was epoxidation product.

of 2-cycloocten-1-ol and 2-cycloocten-1-one were observed. No reaction was observed without catalyst under the same reaction conditions. The turnover frequency (TOF = (mol of products)/(mol of precatalyst) s^{-1}) of 1.8×10^{-1} s^{-1} for TBA-1 was 36.7–476 times those of 3.7×10^{-4}, 1.2×10^{-3}, and 4.8×10^{-3} s^{-1} for TBA-2–TBA-4, respectively (calculated on the basis of mol of precatalyst after a reaction time of 5 min), as shown in Table 1. After 1 h, the TOF of 2.6×10^{-2} s^{-1} for TBA-1 was also 7.2–55.5 times the TOFs of 4.7×10^{-4}, 1.30×10^{-3}, and 3.6×10^{-3} s^{-1} for TBA-2–TBA-4, respectively. The TOF calculated on the basis of the mol of the Ti atom in TBA-1 was 110–476 and 21.6–55.5 times the TOFs of TBA-2–TBA-4 after 5 min and 1 h, respectively. The observed TOFs were compared with those reported for the other homogeneous systems catalyzed by titanium(IV)-substituted POMs, namely, $(Bu_4N)_5[\alpha$-PTiW$_{11}$O$_{40}] \cdot H_2O$ $(4.5 \times 10^{-3}$ s^{-1} after 10 h at 50 °C) and $(4\text{-ddp})_{1.5}$Na$_{5.5}[\alpha$-l,5-PTi$_2$W$_{10}$O$_{40}] \cdot 5H_2O$ (4-ddp = 4-diazodiphenylamine) $(5.9 \times 10^{-3}$ s^{-1} after 10 h at 50 °C) [19].

For the epoxidation of cyclohexene catalyzed by TBA-1 (the ratio of [cyclohexene]/[H$_2$O$_2$] was 0.5), >90% selectivity of the epoxidation products (cyclohexene oxide and cyclohexenediol) suggested that TBA-1 operated primarily via non-radical processes [29,30]. Small amounts of 2-cyclohexen-1-ol and 2-cyclohexen-1-one were observed. The TOF of 1.2×10^{-2} s^{-1} (calculated on the basis of the mol of the catalyst after a reaction time of 4 h) of TBA-1 was ≥ 103 times the TOFs of TBA-2 (no reaction), TBA-3 $(7.6 \times 10^{-6}$ s^{-1}), and TBA-4 $(1.2 \times 10^{-4}$ s^{-1}). The TOF calculated on the basis of the mol of the Ti atom in TBA-1 was 300–3158 times those of TBA-3 and TBA-4. For this reaction, the TOFs have been reported for $(4\text{-ddp})_{1.5}$Na$_{5.5}[\alpha$-l,5-PTi$_2$W$_{10}$O$_{40}] \cdot 5H_2O$ $(9.2 \times 10^{-4}$ s^{-1} with 97% selectivity of epoxidation after 10 h at 50 °C) [19].

It was possible to oxidize not only cycloalkenes (cyclooctene and cyclohexene) but also terminal olefin (1-octene) by TBA-1 ([1-octene]/[H$_2$O$_2$] = 0.7). 1,2-Epoxyoctene was the major product (selectivity of the epoxidation product was >99% for TBA-1). A small amount of heptanal was also formed. The TOF of TBA-1 was 2.8×10^{-3} s^{-1} (calculated after a reaction time of 3 h), which was ≥ 89.4 times the TOFs of TBA-2 (no reaction), TBA-3 $(5.4 \times 10^{-6}$ s^{-1}), and TBA-4 $(3.1 \times 10^{-5}$ s^{-1}). For this reaction, the TOF has been reported for Venturello complex $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ $(1.05 \times 10^{-1}$ s^{-1} after 45 min at 70 °C) [31].

The previous studies on H$_2$O$_2$-based oxidation catalysis by Ti-substituted POMs have indicated that the protons in countercations and/or reaction solutions were crucial for catalytic activities and the formation of an active hydroperoxotitanium species, i.e., the catalytic activities increased with the number of protons in reaction solutions [20,23,32,33]. Thus, the effects of protons in countercations and/or reaction solutions were also investigated, as shown in Fig. 2. Trifluoromethane sulfonic acid (TFSA) was used as the source of protons. The epoxidation of cyclooctene (the ratio of [cyclooctene]/[H$_2$O$_2$] was 0.8) at 25 °C, catalyzed by TBA-1 with different number of protons, was also monitored by gas chromatography.
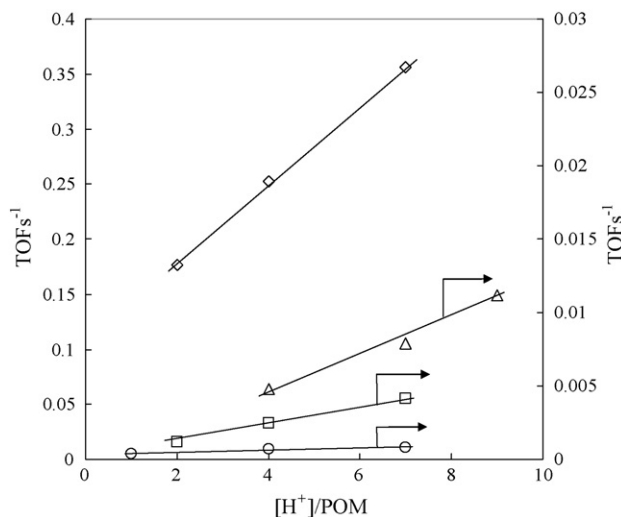

Fig. 2. Effect of the concentration of protons on the catalytic activities for epoxidation of cyclooctene catalyzed by TBA-1 ($\diamondsuit$), TBA-2 ($\bigcirc$), TBA-3 ($\square$), and TBA-4 ($\triangle$). Reaction conditions: TBA-1–TBA-4 20 μmol, 30% H$_2$O$_2$(aq.) 9.72 mmol, 1:1 (v/v) acetonitrile/dichloromethane 30 mL, cyclooctene 7.70 mmol, TFSA 40–120 μmol (two–six protons per POM), reaction temperature 25 °C, reaction time 5 min.

From the acid/base titration, two break points at 2.0 and 2.0 equivalents of added base were observed, which revealed that K-1 had two free protons dissociated from each of the two Ti-OH$_2$ groups and two titratable ligand protons from each of the two Ti–OH groups. Thus, we determined that TBA-1 had two protons that were available for the formation of active hydroperoxotitanium(IV) species. This result was consistent with the elemental analysis.

The number of protons, as shown in Fig. 2, is the sum of the protons in the original compositions and the additional number of protons from TFSA. After 5 min, the TOFs increased with the number of protons for all the complexes. It should be noted that the TOFs of TBA-1 were higher than those of TBA-2–TBA-4 with the same number of protons, and the activities did not exhibit a linear increase with an increase in the number of titanium atoms in POMs. The TOF calculated on the basis of the mol of the Ti atom in TBA-1 was 52.5–354 times those of TBA-2–TBA-4 with four protons. These results revealed that TBA-1, in particular, was the most active. Unfortunately, we were unable to observe the formation of the peroxotitanium(IV)/hydroperoxotitanium(IV) intermediates by a UV–vis spectroscopy because of the lower stability of complex **1** toward H$_2$O$_2$ than those of complexes **2–4**.

4. Conclusions

A novel Ti–O–Ti bonding complex constructed in the monomeric, mono-lacunary α-Keggin polyoxotungstate, i.e., the one host-two guests type POM, $[\{Ti(OH_2)(ox)\}_2(\mu$-O)(α-PW$_{11}$O$_{39}$)]$^{5-}$ (**1**) can act as a precatalyst for the epoxidation of cyclooctene, cyclohexene, and 1-octene with aqueous H$_2$O$_2$ at 25 °C in a homogeneous system. The catalytic activities of complex **1** were considerably higher than those of dimeric mono-, di-, and tri-titanium(IV)-substituted Keggin polyoxotungstates

$[(\alpha\text{-PTiW}_{11}\text{O}_{39})_2\text{O}]^{8-}$, $[(\alpha\text{-1,2-PW}_{10}\text{Ti}_2\text{O}_{38})_2\text{O}_2]^{10-}$, and $[(\alpha\text{-1,2,3-PTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{12-}$. Thus, the isolated μ_2-O Ti–O–Ti site for complex **1** had a significant influence on the catalytic activities for H_2O_2-based oxidation reactions.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.08.052.

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