Alkene epoxidation by hydrogen peroxide in the presence of titanium-substituted Keggin-type polyoxotungstates $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ and $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x = 1$ and 2)

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Abstract

The Ti-substituted Keggin type polyoxotungstates $[PTiW_{11}O_{40}]^{5-}$, $[PTi_2W_{10}O_{40}]^{7-}$, $[PTiW_{11}O_{39}(O_2)]^{5-}$, and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ have been used as catalysts for the epoxidation of alkene with H_2O_2. The alkene epoxidation results from the synergistic interaction between a tungsten-peroxo site with an adjacent Ti-peroxo (η^2) site which acts as an electrophilic center for the alkene on the catalyst. The kinetic feature for the alkene oxidation implies the involvement of $\cdot OH$ radicals with the competition with H_2O_2 dismutation.

Keywords: Ti-substituted Keggin-type polyoxotungstates; Alkene epoxidation; Reaction kinetics; Peroxo Keggin-type polyoxotungstates; Involvement of $\cdot OH$

1. Introduction

$[(PO_4)W_4O_4(O_2)_8]^{3-}$, which has a structure with both terminal (η^2) and bridging ($\eta^2:\eta^1$) peroxo ligands [1], is an excellent catalyst for the alkene epoxidation in a biphasic catalytic system involving $H_3[PW_{12}O_{40}] \cdot 6H_2O$ (or $Na_2WO_4 \cdot 2H_2O$), H_2O_2, and cetylpyridinium chloride [2–4]. The oxidation reaction of alkenes is generally carried out in a two phase water/chlorohydrocarbon mixture where the Keggin-type polyoxotungstate is only a precursor to the true catalyst, $[(PO_4)W_4O_4(O_2)_8]^{3-}$, produced by the reaction between $H_3[PW_{12}O_{40}]$

and H_2O_2 in the aqueous medium [5]. On the other hand, some d-electron-transition-metal (Cr^{III}, Co^{II}, Mn^{II}, Fe^{II}, Ni^{II}, Cu^{II})-substituted Keggin-structural polyoxometalates (TMSP) are known to catalyze the alkene oxidation to epoxide with aqueous H_2O_2 [6–9] in high reactivity and moderate selectivity without degradation of the catalysts. The stable feature of TMSP throughout the reaction is unique, although definitive mechanistic work is lacking on the all TMSP systems. We previously found that the titanium(IV)-disubstituted C_2-symmetric polyoxotungstate $[PTi_2W_{10}O_{40}]^{7-}$ [10,11] is a photocatalyst for the reduction of CO_2 to CH_4 in the presence of alcoholic electron donors and proposed that the kinetic factor for the CO_2 reduction with the $[PTi_2W_{10}O_{40}]^{7-}$ system is the

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formation of the four-electron reduction species $[PTi_2^{III}W_2^{V}W_8O_{40}]^{7-}$ with the configuration

$$Ti^{III}\text{-O-}W^{V}\text{-O-}Ti^{III}\text{-O-}W^{V}\text{-O}$$
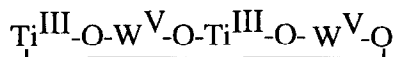
at the $Ti_2^{III}W_2^{V}O_4$ ring in the anion [12]. In addition, we observed that the oxidation of $[PTiW_{11}O_{40}]^{5-}$ and $[PTi_2W_{10}O_{40}]^{7-}$ with H_2O_2 in aqueous solutions leads to the formation of $[PTiW_{11}O_{39}(O_2)]^{5-}$ and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$, respectively, in which the terminal oxygen atom at the TiO_6 octahedral site is replaced by the peroxo ligand with a side-on format [13]. Thus, the fact that the TiO_6 octahedral site in the Ti-substituted Keggin-type polyoxotungstates is an active site for both reduction and oxidation without any degradation of the anion, lets us apply these compounds into the alkene epoxidation with H_2O_2. This paper describes the catalytic activity of the Ti-substituted Keggin type polyoxotungstates $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ and $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x=1$ and 2) for the alkene epoxidation by H_2O_2 (alkene + $H_2O_2 \rightarrow$ alkene epoxide + H_2O) in acetonitrile/dichloromethane (1/1, v/v), which would be ascribed to the involvement of $\cdot$OH radicals with the competition with the H_2O_2 dismutation ($2H_2O_2 \rightarrow 2H_2O + O_2$).

2. Experimental

$K_7[PTi_2W_{10}O_{40}] \cdot 6H_2O$ [10], $[NBu_4]_5[PTiW_{11}O_{40}] \cdot H_2O$ [14], $[Pr_2^iNH_2]_5[PTiW_{11}O_{40}] \cdot 4H_2O$ [13], $[Pr_2^iNH_2]_5[PTiW_{11}O_{39}(O_2)] \cdot 4H_2O$ [13], and $[Pr^iNH_3]_6H[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$ [13] were all prepared and purified according to published procedures. IR spectra agreed with those reported for corresponding compounds. The other materials are referenced in the text or are commercially available.

$[NBu_4]_3[PW_{12}O_{40}]$ was prepared by adding $[NBu_4]Br$ (3 g) into an acidic aqueous solution (100 ml 2 N HCl) of $H_3[PW_{12}O_{40}] \cdot 6H_2O$ (6 g), filtered off, and washed four times with 20 ml of water. White precipitate of $[NBu_4]_3[PW_{12}O_{40}]$ was dried and then recrystallized from acetonitrile. (Found: C, 16.01; H, 3.83; N, 1.21. Calc. for $C_{48}H_{108}N_3O_{40}PW_{12}$: C, 15.99; H, 3.02; N, 1.17%.) $[NBu_4]_5K_2[PTi_2W_{10}O_{40}] \cdot 6H_2O$ was prepared by adding $[NBu_4]Br$ (10 g) into an aqueous solution (160 ml) of $K_7[PTi_2W_{10}O_{40}] \cdot 6H_2O$ (10 g) and then adjusting the resultant solution pH to 5.0 with a 2 N HCl aqueous solution. White precipitate was filtered off, washed twice by water (20 ml), and dried in the air. Recrystallization was done from ethanol/acetonitrile (1/1, v/v). (Found: C, 23.32; H, 4.44; N, 1.74. Calc. for $C_{80}H_{192}N_5O_{46}K_2PTi_2W_{10}$: C, 24.00; H, 4.83; N, 1.75%.)

4-diazodiphenylamine (4-ddp) and 4-diazodiethylaniline (4-dea) salts of polyoxotungstates were prepared by adding an aqueous solution containing (4-ddp)sulfate, or (4-dea)[BF_4] (Daitoh Chemical) into an aqueous solution containing polyoxotungstates. (4-ddp)_3[PW_{12}O_{40}] was prepared by adding (4-ddp)sulfate (0.3 g in 8 ml water) into an acidic aqueous solution (5 ml 2 N HCl) of $H_3[PW_{12}O_{40}] \cdot 6H_2O$ (1 g). Yellow precipitate was filtered off, washed with water, and dried. (Found: C, 12.21; H, 0.87; N, 3.58. Calc. for $C_{36}H_{30}N_9O_{40}PW_{12}$: C, 12.48; H, 0.87; N, 3.64%.) Similarly, (4-dea)_3[PW_{12}O_{40}] was prepared by replacing (4-ddp)sulfate with (4-dea)[BF_4] (0.3 g in 8 ml water). (Found: C,11.33; H,1.23; N,3.95. Calc. for $C_{30}H_{42}N_9O_{40}PW_{12}$: C,10.58; H,1.24; N,3.70%.) Aqueous solutions of $[PTiW_{11}O_{40}]^{5-}$ and $[PTi_2W_{10}O_{40}]^{7-}$ were prepared as follows: a solution of $CH_3CO_2Li \cdot 2H_2O$ (40 g) in water (60 ml) was adjusted to pH 6 with CH_3CO_2H. A solution of $H_3PW_{12}O_{40} \cdot 6H_2O$ (40 g) in water (140 ml) was added to form $[PW_{11}O_{39}]^{7-}$. A 4 ml quantity of $TiCl_4$ was added dropwise with stirring. After the addition, the mixture was refluxed for 30 min, cooled to room temperature, and fil-

tered off. The filtrate (**A**) was used for the preparation of aryldiazonium salts of $[PTiW_{11}O_{40}]^{5-}$. Similarly, $NaH_2PO_4 \cdot 2H_2O$ (6.2 g) was added to a solution of $NaWO_4 \cdot 2H_2O$ (30 g) in water (100 ml). $TiCl_4$ (1.8 ml) was added dropwise with stirring. The mixture was then refluxed for 1 h and followed by filtration. The clear colorless filtrate (**B**) was used for the preparation of aryldiazonium salts of $[PTi_2W_{10}O_{40}]^{7-}$. $(4\text{-ddp})_{4.5}Li_{0.5}[PTiW_{11}O_{40}] \cdot 14H_2O$ was prepared as follows: an aqueous solution (100 ml) of (4-ddp)sulfate (2 g) was added into **A** (200 ml). The yellow precipitate was filtered off, washed with water several times, and dried in the air. (Found: C, 16.80; H, 1.61; N, 4.37. Calc. for $C_{54}H_{73}N_{13.5}O_{54}Li_{0.5}PTiW_{11}$: C,16.72; H, 1.90; N, 4.87%.) $(4\text{-dea})_{4.5}Li_{0.5}[PTiW_{11}O_{40}] \cdot 4H_2O$ was prepared analogously: an aqueous solution (150 ml) of $(4\text{-dea})[BF_4]$ (1.5 g) was added into **A** (80 ml). The yellow precipitate was washed several times with water and dried in the air. (Found: C, 15.01; H, 1.68; N, 5.14. Calc. for $C_{45}H_{71}N_{13.5}O_{44}Li_{0.5}PTiW_{11}$: C, 14.97; H, 1.98; N, 5.24%.) Prepared analogously with **B** were $(4\text{-ddp})_{1.5}Na_{5.5}[PTi_2W_{10}O_{40}] \cdot 5H_2O$ (Found: C,7.47; H, 1.40; N, 1.82. Calc. for $C_{18}H_{25}N_{4.5}O_{45}Na_{5.5}PTi_2W_{10}$: C, 6.94; H, 0.81; N, 2.02%.) and $(4\text{-dea})_3Na_4[PTi_2W_{10}O_{40}] \cdot 9H_2O$ (Found: C, 9.94; H, 1.75; N, 3.48. Calc. for $C_{30}H_{60}N_9O_{49}Na_4PTi_2W_{10}$: C, 10.64; H, 1.79; N, 3.72%).

$(4\text{-ddp})_4[Pr_2^iNH_2][PTiW_{11}O_{39}(O_2)] \cdot H_2O$ was prepared by adding (4-ddp)sulfate (0.4 g in 8 ml water) into an aqueous solution (5 ml) of $[Pr_2^iNH_2]_5[PTiW_{11}O_{39}(O_2)] \cdot 4H_2O$ (1 g). The yellow precipitate was filtered off, washed with water, and dried. (Found: C, 17.80; H, 1.70; N, 5.01. Calc. for $C_{54}H_{58}N_{13}O_{42}PTiW_{11}$: C, 17.71; H, 1.60; N, 4.97%.) Similarly, $(4\text{-ddp})_4[Pr^iNH_3]H_2[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$ was prepared by adding (4-ddp)sulfate (0.7 g in 10 ml water) into an aqueous solution (5 ml) of $[Pr^iNH_3]_6H[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$ (1 g). The orange precipitate was filtered off, washed with water, and dried. (Found: C, 17.58; H,

1.60; N, 5.26. Calc. for $C_{51}H_{54}N_{13}O_{43}PT_2^iW_{10}$: C, 17.50; H, 1.53; N, 5.20%.)

All of the aryldiazonium salts were treated in the dark to avoid their photolysis. The plausible exchange with 4-ddp and 4-dea cations was confirmed by the observable N–N stretching frequencies at about 2164 and 2156 cm^{-1} in IR spectra of the polyoxometalate solids, respectively. The amount of crystal water was determined by thermogravimetric analysis (Rigaku Themoflex TG-DGC). The IR and X-band ESR spectra were recorded on JASCO FT/IR-5000 and JEOL-RE1X X-band spectrometers, respectively. The amount of hydrocarbon derivatives and dioxygen before and after reactions were determined by GC (on a GL Science GL-353 instrument with a TC-WAX capillary 30-m column for the former and a Hitachi 164 GC with a Molecularsieve 5A 1 m column for the latter). GC–MS data on a Hitachi M80 GC–MS spectrometer with PEG-20M column were used for the identification of the oxidation products.
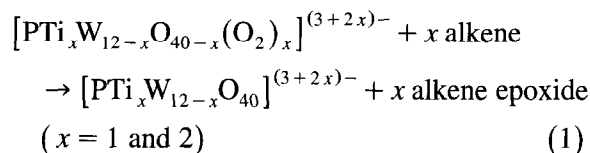
Catalytic oxidation reactions of alkene by H_2O_2 were carried out in a 50 ml Erlenmeyer flask with cooler (with a gum stopper) with a stirring magnetic bar. In a typical oxidation experiment, alkene (4–12 mmol) and catalyst (2–20 μmol) were dissolved in solvent CH_3CN/CH_2Cl_2 (30 ml, 1/1, v/v) and the solution was mixed with 30% H_2O_2 (4–12 mmol). The resulting solution was monophasic. The mixture was stirred at 50°C under reflux conditions, and the progress of the reaction was monitored by GC.

3. Results and discussion

$[NBu_4]^+$, 4-ddp, or 4-dea salt of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ was readily dissolved in CH_3CN/CH_2Cl_2 (1/1, v/v), CH_3CN, or CH_3CN/C_6H_6 (1/1, v/v) solvent within its concentration of 2 mM. The alkene oxidation by H_2O_2 in the presence of $[NBu_4]^+$ salts of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ proceeds with an accompanying coloration of solution to yellow–

orange due to the formation of an η^2-peroxo ligand at the catalyst which would yield $[(PO_4)W_4O_4(O_2)_8]^{3-}$, $[PTiW_{11}O_{39}(O_2)]^{5-}$ and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ for $[PW_{12}O_{40}]^{3-}$, $[PTi_1W_{11}O_{40}]^{5-}$, and $[PTi_2W_{10}O_{40}]^{7-}$ catalysts, respectively [1,13]. The high catalytic activity of $[NBu_4]^+$ salts of Ti-substituted α-Keggin polyoxotungstates was observed as exemplified in Table 1 where the results for the cyclooctene epoxidation at 50°C (for 10 h) are compared with $[NBu_4]^+$, 4-ddp, and 4-dea salts of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$. The amount of 1,2-epoxycyclooctane as the predominant product in the cyclooctene oxidation increased with increasing conversion of cyclooctene and only small amounts of 1,2-cyclooctanediol as a ring-opening product of epoxide was accompanied in less than 10% of epoxycyclooctane. The catalytic activity of the 4-ddp or 4-dea salts of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 0$, 1, 2) increased with an increase in the number of the displacements with Ti atoms, indicating that (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O and (4-dea)$_3$Na$_4$[PTi$_2$W$_{10}$O$_{40}$] · 9H$_2$O are most active in the alkene epoxidation as well as the $[NBu_4]^+$ salts. Parent $[PW_{12}O_{40}]^{3-}$ showed only minimal

catalytic activity, although the $H_3[PW_{12}O_{40}] \cdot 6H_2O$ (20 μmol)/cetylpyridinium chloride (60 μmol) system was used. Epoxidation of cyclooctene also occurred at 69°C in CH_3CN or at 64°C in CH_3CN/C_6H_6 (1/1, v/v) mixture. Since $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 0$, 1, and 2) are oxidized by aqueous H_2O_2 to yield $[(PO_4)W_4O_4(O_2)_8]^{3-}$, $[PTiW_{11}O_{39}(O_2)]^{5-}$ and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ respectively [1,13], we have good reason to believe that the alkene epoxidation in the presence of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 1$ and 2) proceeds via oxo transfer from the $TiO_5(O_2)$ site in the anion to alkene (Eq. (1)), as reported for the active catalysts, $[(PO_4)W_4O_4(O_2)_8]^{3-}$ and $[PCrVW_{11}O_{40}]^{5-}$ [1,15,16].

$$[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-} + x \text{ alkene}$$

$$\rightarrow [PTi_xW_{12-x}O_{40}]^{(3+2x)-} + x \text{ alkene epoxide}$$

$$(x = 1 \text{ and } 2) \tag{1}$$

However, attempted epoxidations of cyclooctene (3 mmol) by (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O (10 μmol) in 30 ml CH_3CN/CH_2Cl_2 (1/1, v/v) solvent did not lead to oxidation of cyclooctene

Table 1

Activity of $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 0-2$) in cyclooctene oxidation

Catalyst	Solvent	Cyclooctene conversion (%)	Cyclooctene epoxide	
			yield (%)	turnover
[NBu$_4$]$_3$[PW$_{12}$O$_{40}$]	a	12	11	32
(4-ddp)$_3$[PW$_{12}$O$_{40}$]	a	16	14	41
(4-dea)$_3$[PW$_{12}$O$_{40}$]	a	12	11	34
H$_3$[PW$_{12}$O$_{40}$] · 6H$_2$O	a	12	12	35
H$_3$[PW$_{12}$O$_{40}$] · 6H$_2$O ^{a}	a	9	9	25
[NBu$_4$]$_5$[PTiW$_{11}$O$_{40}$] · H$_2$O	a	58	54	161
(4-ddp)$_{4.5}$Li$_{0.5}$[PTiW$_{11}$O$_{40}$] · 14H$_2$O	a	31	26	80
(4-dea)$_{4.5}$Li$_{0.5}$[PTiW$_{11}$O$_{40}$] · 4H$_2$O	a	30	21	62
[NBu$_4$]$_5$K$_2$[PTi$_2$W$_{10}$O$_{40}$] · 6H$_2$O	a	59	56	169
(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O	a	60	55	166
(4-dea)$_3$Na$_4$[PTi$_2$W$_{10}$O$_{40}$] · 9H$_2$O	a	59	58	173
(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O	b	80	70	211
(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O	c	56	48	148
(4-dea)$_3$Na$_4$[PTi$_2$W$_{10}$O$_{40}$] · 9H$_2$O	b	43	38	114
(4-dea)$_3$Na$_4$[PTi$_2$W$_{10}$O$_{40}$] · 9H$_2$O	c	52	46	138

20 μmol catalyst, 6 mmol cyclooctene and 12 mmol 30% H_2O_2 were mixed for 10 h in 30 ml solvents of CH_3CN/CH_2Cl_2 (1/1, v/v) at 50°C (a), CH_3CN at 69°C (b), and CH_3CN/C_6H_6 (1/1, v/v) at 64°C (c).
^{a} 60 μmol cetylpyridinium chloride was used as a phase-transfer agent.

within 10 h at 50°C. On the other hand, addition of 6 mmol 30% H_2O_2 to the reaction mixture leads to epoxidation with a high reaction rate; after 6 h the reaction mixture at 50°C contained 0.2 mmol cyclooctene, 2.5 mmol cyclooctene epoxide, and 1.0 mmol O_2, implying that the alkene oxidation (cyclooctene + H_2O_2 → cyclooctene epoxide + H_2O) by (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O competes with the H_2O_2 dismutation ($2H_2O_2$ → $2H_2O + O_2$). Simple $TiCl_4$ and $K_2TiO(C_2O_4)_2 · 2H_2O$ did not show any significant activity at 50°C in the alkene oxidation with H_2O_2.

When the catalytic activity of the (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O was tested on a variety of alkenes in CH_3CN/CH_2Cl_2 (1/1, v/v), generally, the epoxide is the major product with a small amount of 1,2-diol derivatives under the alkene oxidation at 50°C for 10 h. Alkene epoxidation was observed to be a function of the nucleophilicity of the carbon–carbon double bond with increased substitution leading to higher yields. The epoxidation of alkenes occurred in the expected following order of relative activity: cyclooctene > cyclohexene > cyclopentene > 1-dodecene > 1-decene > 1-octene > 1-hexene. Results for cyclooctene, cyclohexene, and 1-octene are exemplified in Table 2 where the catalytic activities of (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O in the oxidations of cyclooctene and cyclohexene are added. The formation of the 1,2-diol deriva-

tives is most clear in the oxidation of cyclohexene with the (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O catalyst where a high selectivity (83%) of 1,2-cyclohexanediol was observed by the known sensitivity to ring-opening of the cyclohexene oxide (selectivity of 3%) which yields a subsequently oxidized product, cyclohexane-1-on-2-ol (selectivity of 14%).

The time dependences of the cyclooctene oxidation by H_2O_2 for (4-ddp)$_{4.5}$Li$_{0.5}$[PTiW$_{11}$O$_{40}$] · 14H_2O and (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O catalysts are shown in Fig. 1 where the results for (4-ddp)$_4$[Pri$_2$NH$_2$][PTiW$_{11}$O$_{39}$(O$_2$)] · H_2O and (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O are also added. A first-order log plot of the time-dependent conversion of cyclooctene indicates the rate of the cyclooctene conversion. It should be noted that an induction period for the oxidation exists in both (4-ddp)$_{4.5}$Li$_{0.5}$[PTiW$_{11}$O$_{40}$] · 14H_2O and (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O systems, while there was no observation of the induction period in both (4-ddp)$_4$[Pr$_2^i$NH$_2$][PTiW$_{11}$O$_{39}$(O$_2$)] · H_2O and (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O systems. Since the possibility of the oxo transfer from the $TiO_5(O_2)$ site in the anion to cyclooctene was ruled out as above described, thus, there is no doubt that the induction period observed for [PTi$_x$W$_{12-x}$O$_{40}$]$^{(3+2x)-}$ ($x = 1$ and 2) reflects the formation of η^2-peroxo ligand at the Ti center in the anion. When the initial rates

Table 2
Oxidation of alkene catalyzed by (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O and (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O

Alkene	Catalyst	Conversion (%)	Product selectivity [a] (turnover)		
			epoxide	1,2-diol	1-on-2-ol
cyclooctene	(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O	59	92 (169)	8 (15)	
	(4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O	94	94 (264)	6 (18)	
cyclohexene	(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O	11	82 (28)	15 (5)	3 (1)
	(4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H_2O	24	3 (1)	83 (60)	14 (10)
1-octene [b]	(4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H_2O	11	82 (26)	18 (6)	

20 μmol catalyst, 6 mmol alkene, and 12 mmol 30% H_2O_2 were mixed at 50°C in 30 ml CH_3CN/CH_2Cl_2 (1/1, v/v) for 10 h.
[a] Percentage of given product of total products.
[b] 48 h of reaction time was employed.

of the conversion for $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ (x = 1 and 2) are estimated from the time dependence following from the induction period, $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ (x = 1 and 2) is always superior to that for corresponding $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ (x = 1 and 2). The initial rate of the conversion hardly depended on the initial concentration of cyclooctene for all systems. The reaction orders for catalyst and H_2O_2 were calculated from the slope of a log observed rate constant against log initial concentrations of catalyst and H_2O_2 for two catalysts $((4\text{-ddp})_4[Pr_2^iNH_2][PTiW_{11}O_{39}(O_2)] \cdot H_2O$ and $(4\text{-ddp})_4[Pr^iNH_3]H_2[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O)$. The results for catalyst and H_2O_2 dependences are shown in Fig. 2(a) and (b), respectively. The reaction, being first order for cyclooctene, showed that the catalyst dependences in the rate law are 0.9 ± 0.1 for $(4\text{-ddp})_4[Pr_2^iNH_2][PTiW_{11}O_{39}(O_2)] \cdot H_2O$ and 0.7 ± 0.1 for $(4\text{-ddp})_4[Pr^iNH_3]H_2[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$. The first-order dependence on catalyst has been observed for the $[(PO_4)W_4O_4(O_2)_8]^{3-}/H_2O_2$ [4]

Fig. 2. Plots of log k (k = initial rate of cyclooctene oxidation) versus log (initial amounts of catalyst (a) and H_2O_2 (b)) for $(4\text{-ddp})_4[Pr_2^iNH_2][PTiW_{11}O_{39}(O_2)] \cdot H_2O$ (▲) and $(4\text{-ddp})_4[Pr^iNH_3]H_2[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$ (●). In (b) the plots for $(4\text{-ddp})_{4.5}Li_{0.5}[PTiW_{11}O_{40}] \cdot 14H_2O$ (△) and $(4\text{-ddp})_{1.5}Na_{5.5}[PTi_2W_{10}O_{40}] \cdot 5H_2O$ (○) are added. Reaction conditions are 2–20 μmol catalyst, 6 mmol cyclooctene, and 12 mmol 30% H_2O_2 for (a) and 20 μmol catalyst, 6 mmol cyclooctene, and 4–20 mmol 30% H_2O_2 for (b) at 50°C in 30 ml CH_3CN/CH_2Cl_2 (1/1, v/v).
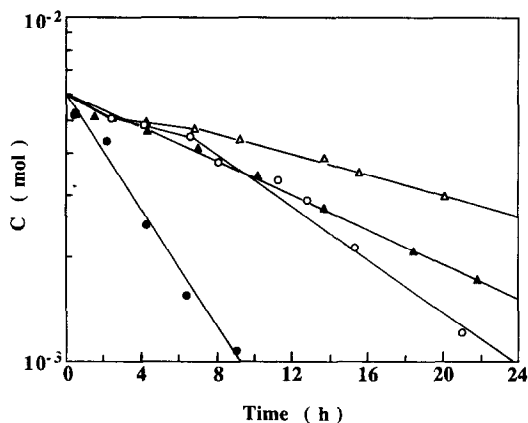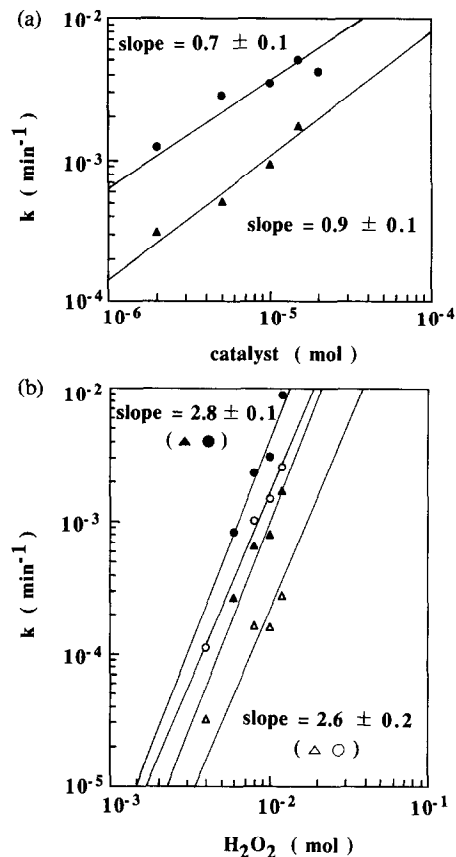

Fig. 1. Kinetic profiles of cyclooctene oxidation as a first-order plot for $(4\text{-ddp})_{4.5}Li_{0.5}[PTiW_{11}O_{40}] \cdot 14H_2O$ (△), $(4\text{-ddp})_4[Pr_2^iNH_2][PTiW_{11}O_{39}(O_2)] \cdot H_2O$ (▲), $(4\text{-ddp})_{1.5}Na_{5.5}[PTi_2W_{10}O_{40}] \cdot 5H_2O$ (○), and $(4\text{-ddp})_4[Pr^iNH_3]H_2[PTi_2W_{10}O_{38}(O_2)_2] \cdot H_2O$ (●) under reaction conditions of 10 μmol catalyst, 6 mmol cyclooctene, and 12 mmol H_2O_2 at 50°C in 30 ml CH_3CN/CH_2Cl_2 (1/1, v/v). C represents the amount (in mol) of cyclooctene.

and $[WZnMn_2^{II}(ZnW_9O_{34})_2]^{12-}/H_2O_2$ systems [17]. The kinetics of the deviation from an exact first-order for the present catalysts suggest the deactivation between active catalysts derived from the $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ (x = 1 and 2) precursor. The H_2O_2 dependence in the rate law was 2.8 ± 0.1 for the two catalysts. A similar dependence (2.6 ± 0.2) of H_2O_2 was observed for $(4\text{-ddp})_{4.5}Li_{0.5}[PTiW_{11}O_{40}] \cdot 14H_2O$ and $(4\text{-ddp})_{1.5}Na_{5.5}[PTi_2W_{10}O_{40}] \cdot$

$5H_2O$, too (Fig. 2(b)). Thus, the result of the kinetic measurements for the cyclooctene epoxidation can be summarized by Eq. (2):

$$\text{rate} \propto \left[[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-} \right.$$

$$\left. (x = 1 \text{ and } 2) \right]^{0.8} [c - C_8H_{16}]^1 [H_2O_2]^{2.8}$$

$$(2)$$

Such a kinetic behavior is different from the $[WZnMn_2(ZnW_9O_{34})_2]^{12-}/H_2O_2$ system [17], in which the H_2O_2 dependence was first order. A multi order in H_2O_2 was reported for the allylic epoxidation with $[SiNb_3W_9O_{37}(O_2)_3]^{7-}$ which showed a H_2O_2 dependence of ~ 1.4 and the catalyst dependence of ~ 0.4 [18]. In the present system the H_2O_2 dependence indicates that H_2O_2 is involved in generating the active catalyst prior to the rate determining step.

The stability of the polyoxotungstates under reaction conditions is important, since the catalytic activity of the simple Keggin $[PW_{12}O_{40}]^{3-}$ has been ascribed to the formation of $[(PO_4)W_4O_4(O_2)_8]^{3-}$ as a result of the solvolytic degradation of $[PW_{12}O_{40}]^{3-}$ by H_2O_2 [1–5]. IR spectra of (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O before and after the cyclooctene oxidation are shown in Fig. 3 where the IR spectrum of (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O is added for comparison. Except that one (at the lowest energy) of three P–O stretching absorptions in the region 1040–1080 cm^{-1} disappears with an accompanying resolution of absorptions at about 600 cm^{-1}, the IR spectrum of (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O in the region 1200–400 cm^{-1} resembles that of (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5H$_2$O which has peaks attributable to C–N, P–O, and W–O vibrations at 1116 (C–N), 1079, 1062, and 1045 (P–O), 948 (W=O), 874 (W–O(μ)–W corner-sharing), and 790 cm^{-1} (W–O(μ)–W edge-sharing). The IR spectrum of the brown oily residue obtained by evaporation after the cyclooctene oxidation (at 50°C for 24 h) for (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O
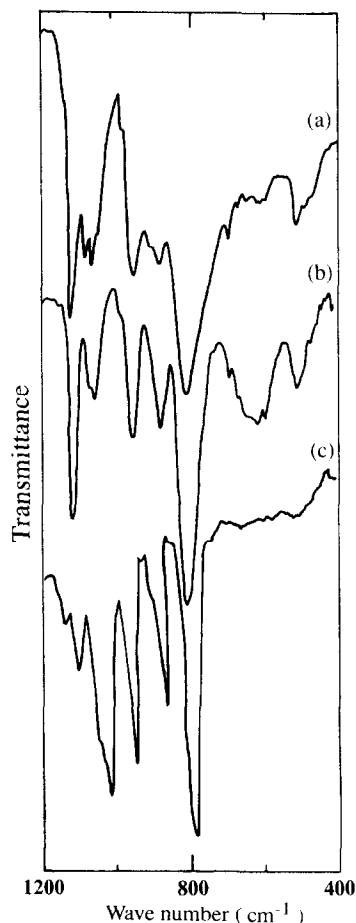
Fig. 3. IR spectra of 4-ddp salts of (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$] · 5 H$_2$O before reaction (a), (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O before reaction (b), and (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O after the cyclooctene oxidation (c) under the reaction conditions of 20 μmol catalyst, 6 mmol cyclooctene, and 12 mmol 30% H$_2$O$_2$ at 50°C for 24 h in 30 ml CH$_3$CN/CH$_2$Cl$_2$ (1/1, v/v).

is similar to that before reaction. Thus, we believe that the Keggin-structural framework for both $[PTi_2W_{10}O_{40}]^{7-}$ and $[PTi_2W_{10}O_{38}(O_2)_2]^{7-}$ catalysts is retained without degradation over a long period (at 50°C for 24 h) of catalytic activity. The solutions were ESR-silent in the steady state throughout the reaction.

The above results indicate that $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x = 1$ and 2) containing the η^2-peroxo ligand at the Ti atom is a precursor of the active intermediate and that the η^2-peroxo $TiO_5(O_2)$ site in the anion is

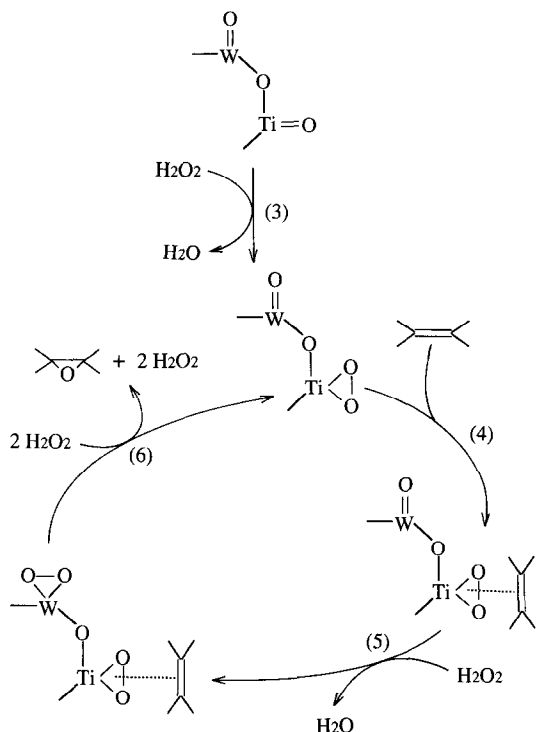Fig. 4. Plausible processes in the alkene epoxidation by H_2O_2 with both $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ and $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x = 1$ and 2) catalysts. In the figure, reaction schemes for both TiO_6 and neighboring WO_6 octahedral sites in the anion are represented.
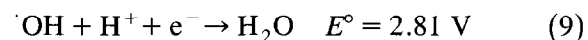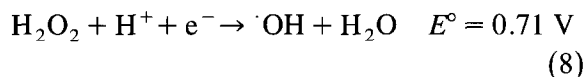
electrophilic enough to allow the alkene to be kept in proximity of the active site. Thus, it is reasonable to assume that the catalytic activity of $[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x = 1$ and 2) is due to the synergistic intramolecular interaction between the Ti-peroxo(η^2) center with a tungsten-peroxo $WO_5(O_2)$ site, which involves further interaction with H_2O_2. Fig. 4 summarizes the plausible processes (Eqs. 3–6) in the alkene epoxidation catalyzed by $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 1$ and 2). A similar mechanism has been proposed for the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}/H_2O_2$ system, where the active catalyst is the tungsten-peroxo intermediate with an adjacent Mn(II) center [17]. However, it should be noted that the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}/H_2O_2$ system indicated the first order dependences on both catalyst and H_2O_2. Formation of such a tungsten-

peroxo intermediate at the WO_6 octahedron site in the anion with H_2O_2 would occur in a manner similar to the $TiO_5(O_2)$ formation at the TiO_6 octahedron in the anion [13]. The multi-order dependence (~ 2.8) on H_2O_2 for the present catalysts lets us set further participation of H_2O_2. As described above the amount of cyclooctene epoxide was higher than that of O_2 in the cyclooctene oxidation. Therefore, the interactions of H_2O_2 with the $-WO_4(O_2)-O-TiO_4(O_2)-$ intermediate would consist of catalytic processes, since the alkene epoxidation exhibiting the multi-order dependence (~ 2.8) on H_2O_2 should represent the overall reaction which provides the equivalence of amounts of both products cyclooctene epoxide and O_2 (Eq. (7)), if this hypothesis is unlikely.

alkene + $3H_2O_2$

$$\rightarrow \text{alkene epoxide} + 3H_2O + O_2 \qquad (7)$$
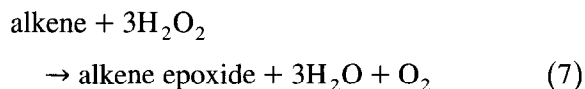
As shown in Fig. 1, (4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$]·H$_2$O exhibited a high rate of cyclooctene oxidation compared with (4-ddp)$_{1.5}$Na$_{5.5}$[PTi$_2$W$_{10}$O$_{40}$]·5H$_2$O. This outlook implies that the rate of the formation of η^2-peroxo ligand at the TiO_6 center (Eq. (3)) is much lower compared with other rates of the complexation with alkene at the $TiO_5(O_2)$ center (Eq. (4)), the formation of peroxo ligand at the W site adjacent to the $TiO_5(O_2)$ center (Eq. (5)), and the epoxidation (Eq. (6)), as reflected by the observable induction period in the $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ ($x = 1$ and 2) system.

A H_2O_2 molecule can produce an $\cdot$OH radical according to Eq. (8) in which E^0 indicates the redox potential in volt versus NHE at pH 0 [19]. Such an $\cdot$OH radical is a strong oxidant as denoted by $E^0 = 2.81$ V (Eq. (9)).

$$H_2O_2 + H^+ + e^- \rightarrow \text{ }\cdot\text{OH} + H_2O \quad E^\circ = 0.71 \text{ V} \tag{8}$$

$$\cdot\text{OH} + H^+ + e^- \rightarrow H_2O \quad E^\circ = 2.81 \text{ V} \tag{9}$$

In the absence of alkene both $[PTi_xW_{12-x}O_{40}]^{(3+2x)-}$ and

$[PTi_xW_{12-x}O_{40-x}(O_2)_x]^{(3+2x)-}$ ($x = 1$ and 2) catalyze the dismutation of H_2O_2 (Eq. (11)) with coupling of the H_2O_2 oxidation to O_2 (Eq. (10)).

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad E° = 0.68\ V \qquad (10)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad\qquad (11)$$
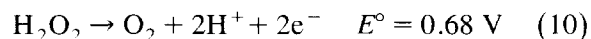
For example, the reaction at 50°C for 7 h for the solution containing 10 μmol [(4-ddp)$_4$[Pr^{i}NH$_3$]H$_2$[PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$] · H$_2$O and 6 mmol 30% H_2O_2 in 30 ml CH_3CN/CH_2Cl_2 (1/1, v/v) gave generation of 2.6 mmol O_2. Such a H_2O_2 dismutation can compete with the alkene oxidation, since the ˙OH radical has a greater tendency to yield epoxide by addition to the double bonds of alkene. Thus, the multi order (~ 2.8) in H_2O_2 in the present systems let us conceive the catalytic participation of H_2O_2 based on the involvement of ˙OH radicals. However, mechanistic details of the oxygen atom transfer in the epoxide formation (Eq. (6)) remain unclear.

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