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H_2O_2-based epoxidation of bridged cyclic alkenes with $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$ in monophasic systems: active site and kinetics

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Abstract

The H_2O_2-based epoxidation of bridged cyclic alkenes in a monophasic system containing low concentrations (<2 mM) of $[Bu_4{}^nN]_4[Pr_2{}^iNH_3]_2H[P\{Ti(O_2)\}_2W_{10}O_{38}]\cdot H_2O$ (**1**) (with two η^2-peroxotitanium sites in the anion) has been studied in search of the catalytically active species involved. ^{31}P NMR spectra of **1**, measured under a variety of conditions, revealed that the active species was not hydroperoxotitanium complex $[P\{Ti(OOH)\}_2W_{10}O_{38}]^{7-}$ or $[P\{Ti(OOH)\}Ti(O_2)W_{10}O_{38}]^{7-}$. The reaction pathways for the alkene epoxidation are discussed to understand the kinetics (especially the initial $[H_2O_2]$ dependence). It was concluded that the net catalytic reaction for the epoxidation occurred through the two-electron oxidation at the hydroperoxotitanium site in the catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Keggin-type hydroperoxotitanium complex; Bridged cyclic alkene epoxidation; H_2O_2; ^{31}P NMR spectroscopy; Ti-active species for epoxidation

1. Introduction

In the course of our studies of the H_2O_2-based epoxidation by Ti^{IV}-substituted Keggin polyoxotungstate catalyst precursors [1,2], we recently found that $[Bu_4{}^nN]_4[Pr_2{}^iNH_3]_2H[P\{Ti(O_2)\}_2W_{10}O_{38}]\cdot H_2O$ (**1**) is an efficient catalyst for the epoxidation of bridged cyclic alkenes such as tricyclo[4.3.0.1^{2,5}]dec-3,7-diene (DCPD), tricyclo[4.3.0.1^{2,5}]dec-7-ene (DH-DCPD), tricyclo[4.3.0.1^{2,5}]dec-7-ene-3,4-dimethylcarboxylate (TCDME) and bis(tricyclo[4.3.0.1^{2,5}]dec-7-ene-3-yl) ether (BTDE) under monophasic condition. Tricyclo[4.3.0.1^{2,5}]decane epoxides and related compounds are useful as starting materials for imaging materials and optical polymer devices [3]. Fig. 1 shows structures of DCPD, DH-DCPD, TCDME and BTDE. The Ti-peroxotungstate anion has also been investigated in the pharmaceutical field as an anti-viral agent against a variety of influenza viruses, as exemplified by $[Pr_2{}^iNH_3]_6H[P\{Ti(O_2)\}_2W_{10}O_{38}]\cdot H_2O$ [4].

We have paid special attention to the chemical structure at the Ti site in a net catalyst for the epoxidation. Fig. 1 also shows structures of $[P\{Ti(O)\}_2W_{10}O_{38}]^{7-}$ (or $[P\{Ti(OH)\}_2W_{10}O_{38}]^{5-}$), $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$ and schematic representation (**A**–**C**) of a structural variety of the Ti sites in Ti-substituted Keggin polyoxotungstates. Subsequently to our X-ray crystallographic characterization of a number of Ti-substituted Keggin polyoxotungstate complexes, $[(C_2H_5)_2NH_2]_4Na[P\{Ti(OH)\}_2W_{10}O_{38}]\cdot 11H_2O$ [5], $[Pr_2{}^iNH_3]_5[PTiW_{11}O_{40}]\cdot 4H_2O$, $[Pr_2{}^iNH_3]_5[P\{Ti

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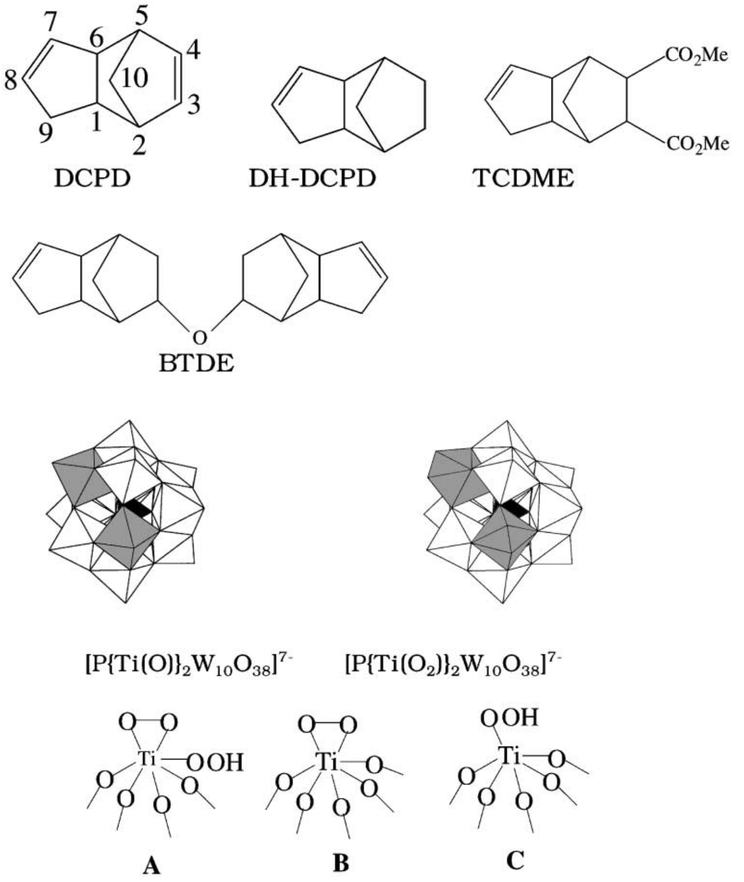


Fig. 1. Structures of pre-catalysts and bridged cyclic alkenes, and schematic representation of a structural variety of peroxo groups at the Ti site in **1**. TiO_6 octahedra and TiO_7 decahedra in polyhedral representations are shaded.

$(O_2)\}W_{11}O_{39}]\cdot 4H_2O$, $[Pr_2{}^iNH_3]_6H[P\{Ti(O_2)\}_2W_{10}O_{38}]\cdot H_2O$ [6] and $K_9H_5[(GeTi_3W_9O_{37})_2O_3]\cdot 16H_2O$ [7], we have shown that these anions function as pre-catalysts for the epoxidation of alkenes with H_2O_2 under the monophasic condition once these are transformed to the putative $Ti(O_2)(OOH)$ multi-peroxo groups at the Ti site (**A** in Fig. 1), although this species, corresponding to one-electron oxidation species of the $Ti(\eta^2\text{-}O_2)$ group with two symmetrically coordinated oxygen centers, has never been isolated [1,2]. In the epoxidation of alkenes by H_2O_2, $[PTiW_{11}O_{40}]^{5-}$ and $[PTi_2W_{10}O_{40}]^{7-}$ anions exhibited an induction period due to the replacement of O^{2-} or OH^- ligands with η^2-peroxo ligands at Ti sites (Ti(O) or Ti(OH) → $(Ti(O_2))$) as a pre-reaction with H_2O_2. Thus, Keggin structural Ti-peroxotungstate anions $[P\{Ti(O_2)\}W_{11}O_{39}]^{5-}$ and $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$, in which Ti atoms show sevenfold coordination by five oxygen atoms and a η^2-peroxo group (**B** in Fig. 1), are effective catalyst precursors for H_2O_2-based epoxidation in homogeneous organic media.

In the known epoxidation reactions, Ti-hydroperoxo or alkylperoxo groups, TiOOR (R=H, alkyl), are generally accepted as oxygen donors, while Ti η^2-peroxo groups are considered inert, in contrast to the η^2-peroxo or bis-peroxo d^0 complexes of Mo, W and Re, which are structurally similar to $Ti(\eta^2\text{-}O_2)$ species and epoxidize alkenes [8–13]. In a recent work on the H_2O_2-based thioether oxidation, a Keggin structural Ti-hydroperoxopolyoxotungstate, $[P\{Ti(OOH)\}W_{11}O_{39}]^{5-}$ as an active catalyst has been suggested (**C** in Fig. 1) [14]. An alternative candidate for Ti-substituted polyoxotungstates as the active catalyst is a heteropolyperoxo compound, $[PO_4\{WO(O_2)_2\}_4]^{3-}$or its structural fragment, $[W_2O_3(O_2)_4]^{2-}$ [15–17], since simple Keggin heteropoly salts $[NBu_4{}^n]_3[PM_{12}O_{40}]$ (M = Mo or W) react with H_2O_2 to yield $[NBu_4{}^n]_3$-$[PO_4\{MO(O_2)_2\}_4]$, and both $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[W_2O_3(O_2)_4]^{2-}$ (for $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ and $[N(C_6H_{13})_4]_2[W_2O_3(O_2)_4]$, respectively) are active catalysts for the epoxidation and *cis*-hydroxylation of alkenes, and the oxidation of alcohols by H_2O_2, especially under phase-transfer conditions with salts containing large lipophilic quaternary ammonium cations [18–20]. Thus, the possibility of the partial degradation of the Ti-peroxo Keggin anions to $[PO_4\{WO(O_2)_2\}_4]^{3-}$ or $[W_2O_3$-$(O_2)_4]^{2-}$ during the alkene epoxidation cannot be excluded. Despite intense experimental works on the H_2O_2-based epoxidation, the chemical structure of the active site of Ti-substituted Keggin polyoxotungstates for the alkene epoxidation is still a matter of controversy, especially for the monophasic system [21–25].

In the present work on the H_2O_2-based epoxidation of the bridged cyclic alkenes with **1**, we describe that an active site is not the hydroperoxotitanium group (**C** in Fig. 1) in $[P\{Ti(OOH)\}_2W_{10}O_{38}]^{7-}$or $[P\{Ti(OOH)\}Ti(O_2)W_{10}O_{38}]^{7-}$, which would be favored in the coexistence of acids such as $H_3PW_{12}O_{40}$ and H_2SO_4 [14], but its two-electron oxidation species, the chemical structure of which is still unclear.

2. Experimental

Orange-colored **1** and white-colored $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ were prepared according to [1,2,26]. The purity of these compounds was checked by IR spectroscopy. Sixty percent aqueous H_2O_2 supplied by Mitsubishi Gas Chemical was used to minimize the content of water in the sample solution so that solubility issues for **1** could be addressed as a monophasic system during the reaction. DCPD, DH-DCPD, TCDME, BTDE, and their oxidation products, tricyclo[4.3.0.1^{2,5}]dec-7-ene-3,4,7,8-diepoxide, tricyclo [4.3.0.1^{2,5}]dec-3,4-epoxide, tricyclo[4.3.0.1^{2,5}]dec-3-ene-7,8-epoxide, tricyclo[4.3.0.1^{2,5}]dec-7,8-epoxide, tricyclo[4.3.0.1^{2,5}]dec-3,4-dimethylcarboxylate-7,8-epoxide, bis(tricyclo[4.3.0.1^{2,5}]dec-7,8-ene-3-yl) ether, (tricyclo[4.3.0.1^{2,5}]dec-7,8-epoxide-3-yl)(tricyclo[4.3.0.1^{2,5}]dec-7-ene-3-yl)ether, tricyclo[4.3.0.1^{2,5}]dec-7-ene-9-ol, tricyclo[4.3.0.1^{2,5}]dec-7-ene-9-one, tricyclo[4.3.0.1^{2,5}]dec-9-ol-3,4-dimethylcarboxylate and tricyclo[4.3.0.1^{2,5}]dec-9-one-3,4-dimethylcarboxylate were supplied by Nissan Chemical Industries. All other reagents were at least analytical grade and were used as-supplied.

IR and electronic spectra were recorded on a JASCO FT/IR-5000 (with KBr pellet) and Hitachi 330 spectrometers, respectively. ^{31}P NMR spectra of samples (at 298 ± 1 K in 5 mm NMR tubes) were measured on a JEOL AL-300 spectrometer at 121.65 MHz using a deuterium lock (CD_3CN or D_2O) and 85% H_3PO_4 as an external standard. All ^{31}P NMR spectral measurements were performed by using a 90° pulse. The spin-lattice relaxation time (T_1 in second) of each species was evaluated by the inversion-recovery method. The scan repetition time was selected to be five times larger than the longest T_1 (15.8 s for −10.8 ppm-peak). Four hundred scans were accumulated (about 11 h) for an acceptable signal-to-noise ratio. A line-broadening factor of 1.0 Hz was applied before FT. Mass spectra were obtained on a Hitachi M80 GC/MS spectrometer with PEG-20M column. GC analyses of organic compounds and oxygen gas were performed on GL Science GL-353 (with a TC-WAX capillary 30 m column at 100 °C) and GC-323 (with molecular sieve 5A 1 m column at 50 °C) instruments, respectively. The amount of H_2O_2 in the samples was determined by adding 2 ml of 9.4 M H_2SO_4 and titrating with a 2.1 N $KMnO_4$ solution in 0.85 M H_2SO_4.

Epoxidation reactions of bridged cyclic alkene by H_2O_2 were carried out in a 50 ml round-bottomed flask, which was charged with **1** (0.20–2.0 mM), 60% aqueous H_2O_2 (0.33–1.67 M), cyclic alkenes (0.1–0.5 M) and *n*-decane (0.5 ml as an internal standard) at 69 °C in 30 ml CH_3CN (or CH_3CN/toluene with 1/1 (v/v) for BTDE). The reaction vessel with a stirring magnetic bar was connected to a −5 °C ethanol/water (1/2, v/v) cooled reflux condenser capped with a rubber stopper to minimize the vapor pressure of CH_3CN during the reaction. Prior to the epoxidation, 20 ml air was removed from head space of the closed vessel by syringe. Aliquots (5 μl) of the monophasic sample solution were analyzed by GC. Epoxides and allylic alcohols (or ketones) as products were identified and quantified by GC–MS and GC. The head space atmosphere was analyzed by withdrawing gas aliquots (2 ml) via a gas-tight syringe. The rates of epoxidation were determined by using the initial rate method. The insertion of syringe into both reaction vessel and its head space was done through septum stoppers.

3. Results

3.1. Epoxidation of bridged cyclic alkenes

Table 1 summarizes the data obtained using four bridged cyclic alkenes. Alkenes in the H_2O_2-free systems were unreactive with **1** under stoichiometric conditions at 69 °C irrespective of the addition of acid (entries 1–4), implying that neither **1** (with the Ti site denoted by **B** in Fig. 1) nor its protonated species (most likely TiOOH-containing species denoted by **C** in Fig. 1) work as an oxygen donor as a net catalyst in the alkene oxidation. Table 1 shows that the extent of conversion of alkene to epoxide was remarkable when 1.0 mM of **1** and 924 mM of H_2O_2 were used (entries 5 and 8–10). The rate of epoxidation was significantly low when $H_3[PW_{12}O_{40}]$ was used as a catalyst precursor compared with that of **1** (entry 11). However, it was much greater than the background conversion that occurred when no polyoxometalate was used (entry 12). $H_3[PW_{12}O_{40}]$ favored the formation of allylic byproducts and other unidentified products, and the mixed $H_3[PW_{12}O_{40}]$/**1** systems increased both selectivity of epoxide and conversion (entries 13–16). Epoxidation of di-olefin (entries 5 and 8) gave the di-epoxide as the major epoxide product after a high conversion of alkenes. Entries 9 and 10 for the oxidation of mono-olefin illustrate the formation of allylic products as byproducts, in contrast to entries 5 and 8 showing no detectable allylic byproducts. The rate of epoxidation of the ester shown in entry 9 was low compared with other bridged cyclic alkenes. As shown in Table 1, conversions (calculated on the basis of the reacted alkenes) of 78–99% and turnover number (mol of epoxides/mol of catalysts used) of up to 196 were obtained for the H_2O_2-based epoxidation of four bridged cyclic alkenes by **1** at 69 °C. There was no detectable product for the reaction at room temperature.

Epoxidation of DH-DCPD was chosen as a model to optimize the conditions and to study the kinetics of epoxidation. Table 2 shows amounts of O_2 as a product of the H_2O_2 dismutation for the DH-DCPD epoxidation together with the decreased amounts for both DH-DCPD and H_2O_2. The amount of H_2O_2 used for the DH-DCPD oxidation, estimated by subtracting the amount (equal to twofold amounts of O_2) of H_2O_2 used for O_2 evolution (due to the H_2O_2 dismutation) from that for the overall reaction, is fairly close to the amount of DH-DCPD used for the oxidation. This indicates that **1** catalyzes both H_2O_2-based oxidation of alkene and H_2O_2 dismutation at 69 °C.

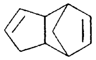
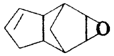
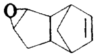
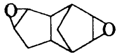
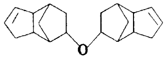
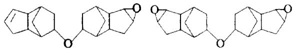
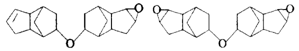
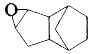
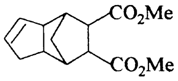
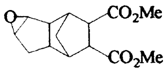
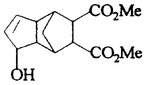
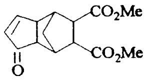
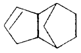
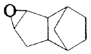
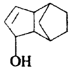
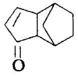
3.2. Rate law studies

Fig. 2(a), (b) and (c) shows plots of the formation of DH-DCPD epoxide as functions of time with a variety of concentrations of **1**, DH-DCPH and H_2O_2, respectively, at 69 °C in 30 ml CH_3CN. The time-dependent yields of DH-DCPD epoxide showed an approximately linear relationship at the initial 10 h, which allows to estimate the initial rate (r) of the product formation. The reaction orders for **1**, DH-DCPH and H_2O_2 were calculated from the slope of a $\log(r)$ against log(initial concentrations of **1**, DH-DCPD and H_2O_2). The results for the DH-DCPD epoxide formation are shown in Fig. 3. The kinetic study showed that the dependencies of the epoxide formation rate on concentrations of **1**, DH-DCPD and H_2O_2 were 0.47 ± 0.01, 1.06 ± 0.02 and 1.99 ± 0.17, respectively:

$$r = \frac{\mathrm{d[epoxide]}}{\mathrm{d}t} = k_3[\mathbf{1}]^{0.47\pm0.01}[\mathrm{alkene}]^{1.06\pm0.02}[\mathrm{H_2O_2}]^{1.99\pm0.17} \tag{1}$$

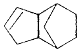
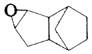
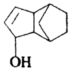
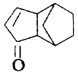
It should be recalled that the H_2O_2-based epoxidation with stable polyoxometalates (for instance, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$) indicated a first-order dependence on both H_2O_2 and catalyst [27]. Multiple orders in the H_2O_2 dependence for the H_2O_2-based alkene epoxidation are characteristic of the Ti-peroxo Keggin polyoxotungstate pre-catalysts: ~2.8, ~2.3 and ~2.0 for the aryldiazonium salt of $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$/cyclooctene, **1**/cyclooctene and **1**/DH-DCPD systems, respectively [1,2]. This implies that the one-electron oxidation intermediate produced by the reaction of **1** as a pre-catalyst with H_2O_2 is involved in the generation of the active catalyst prior to the rate-determining step

Table 1
Epoxidation of bridged cyclic alkenes at 69 °C in monophasic CH_3CN solutions[a]

Entry	**1** (mM)	Substrate (mM)	H_2O_2 (mM)	Reaction time (h)	H_2SO_4 (mM)	Products (mM)				Conversion in % (turnover)
		 DCPD							Others	
1	33	33	0	1	–	0				–
2	33	33	0	10	–	0				–
3	33	33	0	1	66	0				–
4	33	33	0	10	66	0				–
5	1.0	198	924	15	–	46	18	130		99.2 (196)
6	1.0	198	90	15	–	2.6	0.65	0		1.6 (3)
7	1.0	198	30	15	–	2.0	0.33	0		1.2 (2)
		 BTDE								
8	1.0	99	924	15	–	21	46	15		97.4 (89)
		 TCDME								
9	1.0	198	924	30	–	128	13	10		78.9 (129)
		 DH·DCPD								
10	1.0 ($H_3PW_{12}O_{40}$)	193	924	30	–	171	10	6	–	97.6 (173)
11	1.0	198	924	30	–	22	17	19	9	34 (22)
12	0 ($H_3PW_{12}O_{40}$/**1**)	198	924	30	–	0	0	0	3.9	2.0
13	0.2/0.18	198	924	30	–	63	18	19	46	74 (158)
14	0.2/0.46	198	924	30	–	121	25	28	7	92 (181)
15	0.2/0.69	198	924	30	–	119	14	29	32	98 (133)
16	0.2/0.92	198	924	30	–	103	18	25	48	98 (84)

[a] A mixed CH_3CN/toluene solvent (with 1/1, v/v) was used for the BTDE epoxidation.

Table 2
Epoxidation of DH-DCPD and dismutation of H_2O_2 at 69 °C in monophasic CH_3CN solutions

Entry	**1** (mM)	Substrate (mM)	H_2O_2 (mM)	Reaction time (h)	H_2SO_4 (mM)	Products (mM)					–[DH-DCPD] (mM)	–[H_2O_2](mM)
		 DH-DCPD							Others	O_2 (mM)		
1	1.0	185	1650	30	–	159	7	5	11	44	183	271
2	1.0	185	1320	30	–	142	8	4	29	49	183	281
3	1.0	193	924	30	–	171	10	6	–	38	188	264
4	1.0	95	924	30	–	51	3	2	30	109	86	307

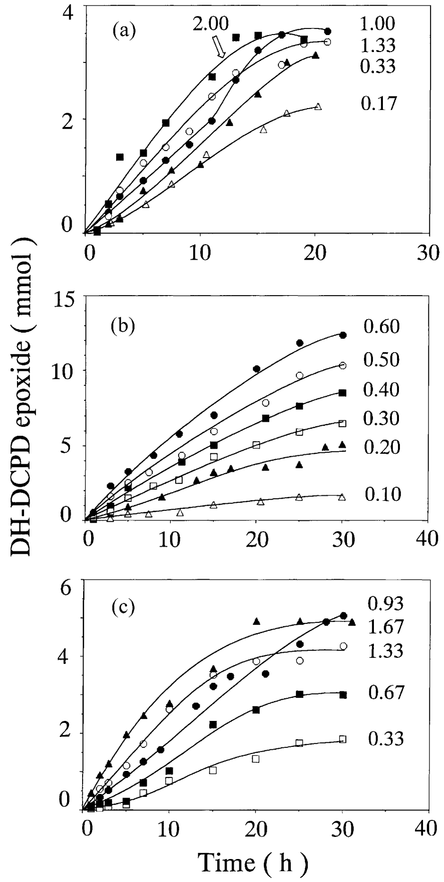


Fig. 2. Time-dependent yields of DH-DCPD epoxide for (0.17–2.0 mM) **1**/0.2 M DH-DCPD/0.93 M H_2O_2 (a), 1.0 mM **1**/(0.10–0.60 M) DH-DCPD/0.93 M H_2O_2 (b), and 1.0 mM **1**/0.20 M DH-DCPD/(0.33–1.67 M) H_2O_2 (c) systems in CH_3CN (30 ml) at 69 °C. Numbers in (a)–(c) indicate initial concentrations of **1** (in mM), DH-DCPD (in M) and H_2O_2 (in M), respectively.

of the epoxidation. Interestingly, the catalyst dependence (~0.5) for the **1**/DH-DCPD system is different from that (~0.9) for the **1**/cyclooctene system [2]. A similar pre-catalyst dependence has been reported for the allylic epoxidation with $[Si\{Nb(O_2)_3W_9O_{37}\}]^{7-}$ (~0.4 and ~1.4 for pre-catalyst and H_2O_2 dependencies, respectively) [28].

3.3. ^{31}P NMR studies

Fig. 4 shows ^{31}P NMR spectral change of **1** (1.0 mM) in CD_3CN on a variety of H_2O_2 concentration. The ^{31}P NMR spectrum of **1** showing a singlet peak at $\delta = -10.8$ ppm (Fig. 4(a)) irrespective of the presence of DH-DCPD exhibits a downfield-shift on the addition of H_2O_2. The extent of the downfield-shift corresponds to the amount of H_2O_2: $\delta \approx -10.3$, -9.6 and -9.4 ppm for $[H_2O_2] = 50$ mM, 0.93 and 2.80 M, respectively (Fig. 4(b)–(d)). The 21 h reaction of **1** (1.0 mM) with H_2O_2 (2.80 M) at 69 °C in CD_3CN resulted in two ^{31}P NMR line peaks at $\delta \approx -10.2$ and -11.1 ppm (Fig. 4(e)). The singlet lines at $\delta \approx -9.4$ to -10.3 ppm in the presence of H_2O_2 were also observed upon addition

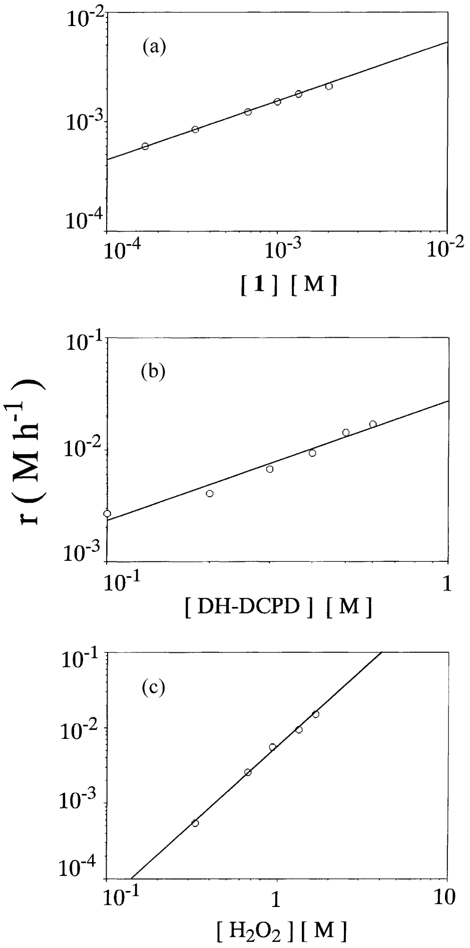


Fig. 3. Plots of log(r = observed rate at initial stage of epoxide formation) against log(initial concentrations of **1** (a), DH-DCPD (b) and H_2O_2 (c)).

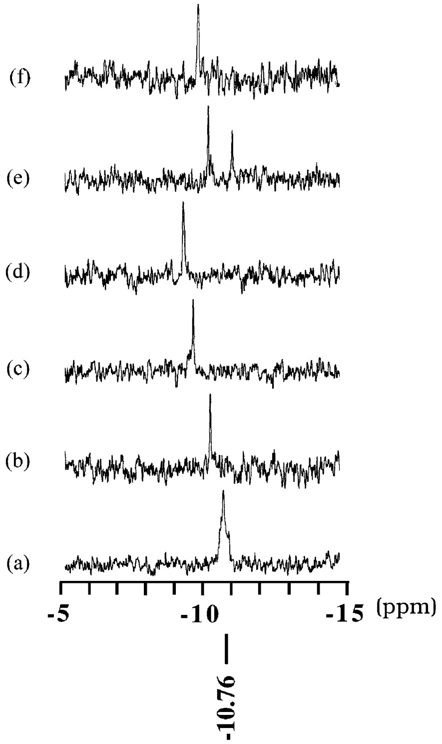


Fig. 4. ^{31}P NMR spectral change of **1** (1.0 mM) in CD_3CN on a variation of H_2O_2 concentration: (a) without H_2O_2, (b) 50 mM, (c) 0.93 M, (d) 2.80 M, (e) after 21 h at 69 °C for (c), (f) **1** (1.0 mM) + H_2SO_4 (10 mM) without H_2O_2.

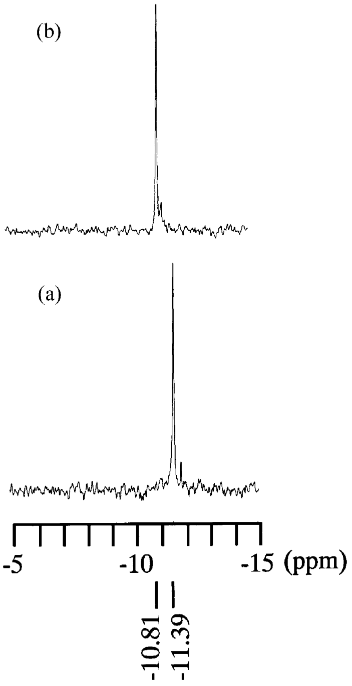


Fig. 5. ^{31}P NMR spectral change of $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ (1.0 mM) by the reaction with H_2O_2 (0.93 M) in D_2O: (a) no H_2O_2 and (b) H_2O_2 (0.93 M).

of H^+ (H_2SO_4) to the CD_3CN solution containing **1** (Fig. 4(f)), and assigned to the hydroperoxotitanium and its related (with different proton content) species (**C** in Fig. 1) due to the similarity of the ^{31}P NMR spectral change of $[PTi(O_2)W_{11}O_{39}]^{5-}$ [14]. Fig. 5 shows ^{31}P NMR spectral change of $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ (1.0 mM) in D_2O under the treatment with H_2O_2 (0.93 M). As shown in Fig. 5, the reaction of $[PTi_2W_{10}O_{40}]^{7-}$ with H_2O_2 to yield $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$ in D_2O indicated the change of δ value from −11.4 to –10.8 ppm. In conjunction with the fact that $[Bu_4N]_4K_2H[PTi_2W_{10}O_{40}]\cdot 6H_2O$ showed a ^{31}P NMR line peak at $\delta \approx -11.4$ ppm in CD_3CN [2]; therefore, the observable line peak at $\delta \approx 11.1$ ppm in Fig. 4(e) reflect the deoxygenation of **1** to the parent species $[PTi_2W_{10}O_{40}]^{7-}$.

Fig. 6 shows ^{31}P NMR spectral change of **1** (1.0 mM) on the progress of epoxidation of DH-DCPD (0.19 M) with H_2O_2 (0.93 M) at 69 °C in CD_3CN. The epoxidation of DH-DCPD diminished the species at $\delta \approx -9.4$ to -10.3 ppm with an accompanying growth of the $\delta \approx -11.1$ ppm species. The epoxidation of DH-DCPD still proceeds after 20 h at 69 °C (Fig. 2(d)), when the $\delta \approx -9.4$ to -10.3 ppm species was no longer observed. When DH-DCPD was replaced by DCPD, which has a higher rate for epoxidation, the $\delta \approx -9.6$ ppm line disappeared after 12 h. The feature of the ^{31}P NMR chemical shift for the epoxidation of cyclooctene (0.20 M) in the 1.3 mM **1**/0.92 M H_2O_2/CD_3CN system was the same as for the DH-DCPD epoxidation.

The above results of ^{31}P NMR spectra of **1** under various conditions in CD_3CN indicate that $\delta \approx -11.1$, 10.8 and −9.4 to -10.3 ppm species can be identified as $[PTi_2W_{10}O_{40}]^{7-}$, $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$ and $[P\text{-}\{Ti(OOH)Ti(O_2)\}W_{10}O_{38}]^{7-}$ and/or $[P\{Ti(OOH)\}_2\text{-}W_{10}O_{38}]^{7-}$, respectively. These species correspond to the formation of –O–Ti(O)–O–, **B** and **C** groups at the Ti sites, respectively. In connection with a large pK_a value (=11.8 in water at 20 °C) for H_2O_2

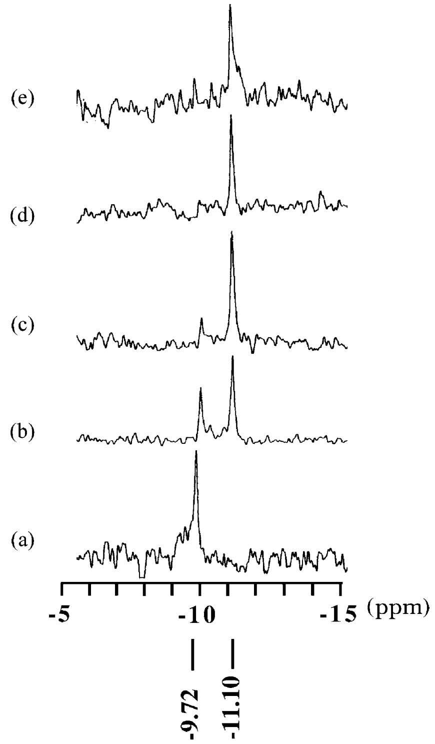


Fig. 6. ^{31}P NMR spectral change of **1** (1.0 mM) during the DH-DCPD (0.20 M) epoxidation with H_2O_2 (0.93 M) at 69 °C in CD_3CN: (a) 0 h, (b) 5 h, (c) 10 h, (d) 20 h, and (e) 30 h.

which is comparable with the third dissociation constant of H_3PO_4 [29], the strong dependence of the ^{31}P NMR chemical shift for the hydroperoxotitanium complex at $\delta \approx -9.4$ to -10.3 ppm on the H_2O_2 concentration suggests that the Ti(OOH) sites of $[P\{Ti(OOH)Ti(O_2)\}W_{10}O_{38}]^{7-}$ and/or $[P\{Ti(OOH)\}_2W_{10}O_{38}]^{7-}$ in the sample solutions should have a more complicated structure, probably associated with the aggregates of H_2O_2 molecules.

4. Discussion

The hydroperoxotitanium complex (**C** in Fig. 1) has been proposed as an active intermediate for the H_2O_2-based thioether oxidation by Hill's group [14]. However, this species is not active for the alkene epoxidation in the present system, since the corresponding hydroperoxotitanium species, which was formed in the presence of acids (Fig. 4(f)), did not oxidize alkenes under stoichiometric conditions (entries 3 and 4 in Table 1). As far as the H_2O_2-based oxidation of methylphenyl thioether (MPS) to methylphenyl sulfoxide (MPSO) with **1** at 69 °C was done, furthermore, the most efficient oxidation to sulfoxide occurred in acid- and **1**-free background system. Table 3 shows amounts of MPSO product for the H_2O_2-based oxidation of MPS at 69 °C with and without acid. The results in Table 3 reveal that the hydroperoxotitanium complex favored by the addition of acid is not a net catalyst for this type of oxidation, in contrast to a previous conclusion that the hydroperoxotitanium complex $[P\{Ti(OOH)\}W_{11}O_{39}]^{4-}$ is the active catalyst for the H_2O_2-based MPS oxidation [14].

The reaction between **1** (of high concentration of >10 mM) and H_2O_2 in CH_3CN at 69 °C brought about the partial degradation of **1** to $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (showing multiplet lines at $\delta \approx +4$ ppm in ^{31}P NMR spectra) [2]. This let us conceive the possibility of degradation product as the net active catalyst in the system containing low concentrations (<2 mM) of **1** under monophasic conditions. However, the second-order dependence of H_2O_2 for the epoxide reaction rate excludes this possibility, since a zero-order dependence of H_2O_2 should be expected if this possibility were operative [30]. Furthermore, ^{31}P NMR spectra of **1** after the H_2O_2-based epoxidation of alkenes revealed that the Keggin structure of the catalyst precursor was still intact (Fig. 6), as also

Table 3
Oxidation of MPS to MPSO with H_2O_2[a]

Entry	MPS (M)	H_2O_2 (M)	**1** (mM)	$HClO_4$ (mM)	Reaction time (h)	Product (MPSO) (M)
1	0.5	0.2	0.5	0	16.5	0.042
2	0.5	0.2	0.5	0.75	17	0.058
3	0.5	0.2	0	0	17	0.174

[a] All experiments were carried out at 69 °C in CH_3CN (30 ml), in the same way as for the epoxidation of the bridged cycle alkenes by H_2O_2.

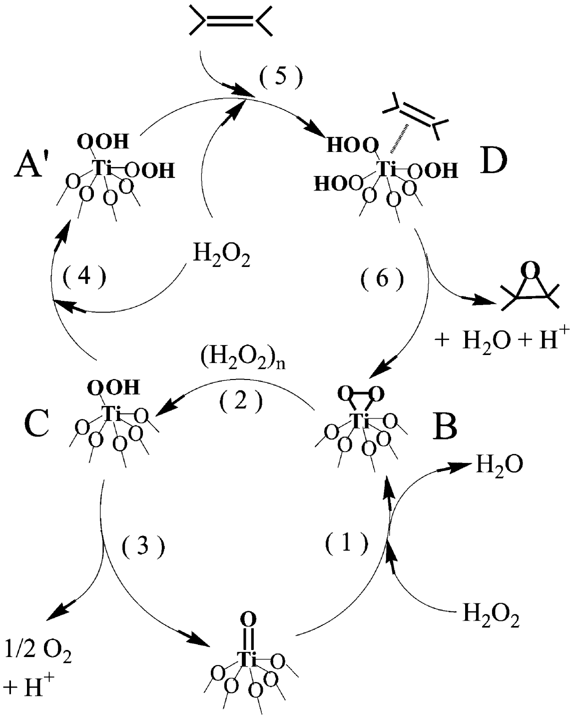


Fig. 7. Structural change of the Ti site in the alkene epoxidation by H_2O_2 with **1**. **A**′ and **D** indicate one- and two-electron oxidation states of **C**, although precise structures of these intermediates are still unclear.

suggested previously by the IR spectra [1,2]. The fact that the reaction of $H_3PW_{12}O_{40}$ (1.0 mM) with H_2O_2 (0.93 M) in CD_3CN at 69 °C for 30 h resulted in no significant change of ^{31}P NMR chemical shift (at $\delta \approx -14.0$ ppm) also supports that the degradation of the pre-catalyst (of low concentrations of <2 mM) to $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is unlikely.

The reaction pathways for the alkene epoxidation which are in agreement with the above experimental results are shown in Fig. 7 where the chemical changes at the Ti site for the anion are schematically represented with reaction steps (1)–(6). In conjunction with the above ^{31}P NMR results of **1**, a second-order dependence of H_2O_2 for the epoxide reaction rate (Eq. (1)) leads to the conclusion that the active intermediate (**D** in Fig. 7) for the alkene epoxidation is formed by a two-electron oxidation of the hydroperoxotitanium complex $[P\{Ti(OOH)Ti(O_2)\}W_{10}O_{38}]^{7-}$ and/or $[P\{Ti(OOH)\}_2W_{10}O_{38}]^{7-}$. Such a Ti(OOH) group (**C** in Figs. 1 and 7) showing ^{31}P NMR lines at $\delta \approx -9.4$ to -10.3 ppm is assumed to be produced by the interaction of **1** with a H_2O_2 aggregate and stabilized (Eq. (2) and step (2) in Fig. 7):

$$\begin{aligned}&\mathrm{-W{-}O{-}Ti(O_2){-}O{-}W{-}} + (H_2O_2)_n\\&\quad\rightarrow \mathrm{-W{-}O{-}Ti(OOH){-}O{-}W{-}} + (HO_2{}^-)(H_2O_2)_{n-1}\end{aligned}\tag{2}$$

In a previous study on the cyclooctene epoxidation, we proposed that the alkene epoxidation results from two-electron oxidation intermediate of **1** through one-electron oxidation species (hypothetical $Ti(O_2)$ (OOH)-species denoted by **A** in Fig. 1) of the alkene-coordinated **1** [2]. The two successive oxidations (via one-electron oxidation state **A**′) of the hydroperoxo complex by two H_2O_2 molecules implies that each H_2O_2 molecule acts as one-electron oxidant at the Ti(OOH) site of **1** (steps (4) and (5) in Fig. 7). The rate dependence of a first-order in alkene suggests an involvement of alkene in the two-electron oxidation of the hydroperoxotitanium complex, irrespective of the coordination of alkene to **1** ($K = 1.70 \times 10^3\ M^{-1}$ and $\varepsilon_{396} = 2.36 \times 10^3\ M^{-1}\ cm^{-1}$ for DCPD at room temperature, that were obtained by Ketelaar's method of analysis) [2,31]. The rate dependence of a half-order of **1** is rationalized by the thermal deactivation of **C** in the hydroperoxo complex to $[PTi_2W_{10}O_{40}]^{7-}$which corresponds to the disproportionation of **C** species (Eq. (3) and step (3) in Fig. 7), as $[PTi_2W_{10}O_{40}]^{7-}$ in CD_3CN was produced at 69 °C in the presence of H_2O_2 (Fig. 4(e)), not at room temperature within 30 h:

$$\begin{aligned}&2\{\mathrm{-W{-}O{-}Ti(OOH){-}O{-}W{-}}\}\\&\quad\rightarrow 2\{\mathrm{-W{-}O{-}Ti(O){-}O{-}W{-}}\} + O_2 + 2H^+\end{aligned}\tag{3}$$

The formation of the parent $[PTi_2W_{10}O_{40}]^{7-}$ anion also occurred after the epoxide formation (step (6) in Fig. 7) from the active intermediate (**D** in Fig. 7), as indicated by the ^{31}P NMR results (Fig. 6(b)–(e)). Thus, the Ti(O) groups in the parent anions were converted again to **C** after the formation of **B** (step (1) in Fig. 7) in the presence of excess amounts of H_2O_2, as also supported by the results of $[PTi_2W_{10}O_{40}]^{7-}$ in aqueous solutions (Fig. 5).

The precise structure of the active intermediate (**D** in Fig. 7) as a two-electron oxidation species for the H_2O_2-based oxidation of alkenes is still unclear. As for the two-electron oxidation of **1**, it can be recalled that the cyclic voltammogram of **1** in the absence of alkene showed a quasi-reversible couple at about 0.30 V vs Ag/AgCl in CH_3CN in contrast to the coexistence of alkenes which led to the irreversible oxidation probably due to the formation of alkene oxide [2]. Then, the cyclic voltammograms for the Ti site in **1** suggests that the $Ti(O_2)$ group (**B**) in **1** acts as an electrochemical two-electron oxidation catalyst for the alkene oxidation at about 0.30 V vs Ag/AgCl in CH_3CN, although the electrochemical activity at **B** is much lower than at W sites in **1**.

In steady-state conditions for the thermally activated **C**

$$k_2[\mathbf{B}][H_2O_2] = k_3[\mathbf{C}]^2 \quad (4)$$

the reaction rate for the epoxidation, *r*, is

$$r = k_5[\mathbf{A}'][H_2O_2][\text{alkene}] \quad (5)$$

where each rate constant (k_n) corresponds to that of each reaction step (n) in Fig. 7. Since the concentration of **A**′ site ([**A**′]) in the system would be proportional to the steady-state concentration of the thermally activated **C**:

$$r = \alpha \left(\frac{k_2}{k_3}\right)^{1/2} k_5[\mathbf{B}]^{1/2}[H_2O_2]^{3/2}[\text{alkene}] \quad (6)$$

where α is the probability of the conversion of the thermally activated **C** into **A**′ site in **1**. Eq. (6) is in good agreement with the experimental data (Eq. (1)) on the dependence of **1** and alkene concentrations. Eq. (6) predicts that the multiplicity of the H_2O_2 dependence of the rate of alkene epoxidation is altered at the range 2.5–1.5, on whether H_2O_2 acts as one- or two-electron oxidant at the **C** site, since α is proportional to a first-order of $[H_2O_2]$ in the former case. Therefore, the second-order of H_2O_2 (Eq. (1)) implies the dual oxidations at the **C** site in **1** by H_2O_2. Thus, the variant multi-order of H_2O_2 in Eq. (6) seems to demonstrate the results of the H_2O_2-based epoxidation with Keggin peroxotungstate pre-catalysts (∼2.8, ∼2.3 and ∼2.0 for the aryldiazonium salt of $[P\{Ti(O_2)\}_2W_{10}O_{38}]^{7-}$/cyclooctene, **1**/cyclooctene and **1**/DH-DCPD systems, respectively [1,2] and ∼1.4 for the allylic epoxidation with a use of $[Si\{Nb(O_2)\}_3W_9O_{37}(O_2)_3]^{7-}$ [28]). Approximate half dependence (∼0.4) of pre-catalyst on the epoxidation rate in the allylic epoxidation with a use of $[Si\{Nb(O_2)\}_3W_9O_{37}]^{7-}$ is noted [28], which also suggests the occurrence of disproportionation of a Nb(OOH) hydroperoxoniobium group in a way similar to Eq. (3) prior to the rate-determining step of the epoxidation.

In conclusion, the H_2O_2-based epoxidation of bridged cyclic alkenes in a monophasic system containing low concentrations (<2 mM) of $[Bu_4{}^nN]_4[Pr_2{}^iNH_3]_2H[P\{Ti(O_2)\}_2W_{10}O_{38}] \cdot H_2O$ (**1**) (with two η^2-peroxotitanium sites in the anion) was studied in search of the catalytically active species involved. ^{31}P NMR spectra of **1**, measured under a variety of conditions, indicated that the net catalytic reaction for the H_2O_2-based alkene epoxidation by a use of the T^{IV}-substituted Keggin polyoxotungstate catalyst precursors occurred through the two-electron oxidation (**D** in Fig. 7) at the hydroperoxotitanium site (**C** in Fig. 7) in the catalyst. The kinetic analysis for the epoxidation demonstrated that the multiple orders (2.5–1.5) in the $[H_2O_2]$ dependence of the epoxidation rate arose from the dual oxidations (as one- and two-electron oxidants) of H_2O_2 at the **C** site.

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References

[1] T. Yamase, E. Ishikawa, Y. Asai, S. Kanai, J. Mol. Catal. A 114 (1996) 237.
[2] E. Ishikawa, T. Yamase, J. Mol. Catal. A 142 (1999) 61.
[3] J.C. Wilson, F.L. Hamb, J. Polym. Soc. 10 (1972) 3191.
[4] S. Shigeta, S. Mori, J. Watanabe, S. Soeda, K. Takahashi, T. Yamase, Antimicrob. Agents Chemother. 41 (1997) 1423.
[5] T. Ozeki, T. Yamase, Acta Crystallogr. C 47 (1991) 693.
[6] T. Yamase, T. Ozeki, S. Motomura, Bull. Chem. Soc. Jpn. 65 (1992) 1453.
[7] T. Yamase, T. Ozeki, H. Sakamoto, S. Nishiya, A. Yamamoto, Bull. Chem. Soc. Jpn. 66 (1993) 103.
[8] T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974.
[9] H. Mimoun, I.S. de Roch, L. Sajus, Tetrahedron 26 (1970) 37.
[10] M.G. Clerici, P. Ingallina, J. Mol. Catal. 140 (1980) 71.

[11] M.G. Finn, K.B. Sharpless, J. Am. Chem. Soc. 113 (1991) 113.

[12] C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197.

[13] I.V. Yudanov, P. Gisdakis, C.D. Valentin, N. Rösch, Eur. J. Inorg. Chem. 12 (1999) 2135.

[14] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovkaya, L.A. Kovaleva, M.A. Fedotov, V.A. Grigoviev, C.L. Hill, Inorg. Chem. 39 (2000) 3828.

[15] C. Venturella, R. D'Aloisio, J.C.J. Bart, M. Ricci, J. Mol. Catal. 32 (1985) 107.

[16] C. Venturella, R. D'Aloisio, J. Org. Chem. 53 (1988) 1553.

[17] A.C. Dengel, W.P. Griffith, B.C. Parkin, J. Chem. Soc., Dalton Trans. (1993) 2683.

[18] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, T. Ogawa, J. Org. Chem. 53 (1988) 3587.

[19] A.J. Bailey, W.P. Griffith, B.C. Parkin, J. Chem. Soc., Dalton Trans. (1995) 1833.

[20] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681.

[21] N.J. Crano, R.C. Chambers, V.M. Lynch, M.A. Fox, J. Mol. Catal. A 114 (1996) 65.

[22] K. Nomiya, Y. Arai, M. Takashi, T. Takayama, H. Weiner, T. Nagata, J.A. Widergan, R.J. Finke, Inorg. Chim. Acta 300–302 (2000) 285.

[23] M. Schwegler, M. Floor, H. van Bakkum, Tetrahedron Lett. 29 (1988) 823.

[24] N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Likhobov, Kinet. Katal. 33 (1992) 516.

[25] O.A. Rholdeeva, G.M. Maksimov, M.A. Fedotov, V.A. Grigoriev, React. Kinet. Catal. Lett. 53 (1994) 331.

[26] P.T. Domaille, W.H. Knoth, Inorg. Chem. 22 (1983) 818.

[27] R. Neumann, M. Gara, J. Am. Chem. Soc. 117 (1995) 5066.

[28] M.W. Droego, R.G. Finke, J. Mol. Catal. 69 (1991) 323.

[29] N.N. Greenwood, A. Earnshaw, Chemistry of Elements, Pergamon Press, Oxford, 1984, p. 747.

[30] Z. Raciszewski, J. Am. Chem. Soc. 82 (1960) 1267.

[31] J.A.A. Ketelaar, C. vande Stolpe, A. Goudsmit, W. Dzcubas, Rec. Trav. Chim. 71 (1952) 1104.